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# Multistage Membrane Separation Processes for the Continuous Fractionation of Solutes Having Similar Permeabilities

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A new cascade configuration for the continuous membrane fractionation of solutes having similar permeabilities is proposed. In this scheme, solute selectivity is amplified by combining a concentrator and several mass exchangers (e.g., a reverse osmosis unit and hollow fiber dialyzers) to achieve a desired degree of separation. Separation efficiency of the new cascade is compared with that of a conventional counter-current cascade.

## SCOPE

Liquid-phase membrane separation processes (such as dialysis, reverse osmosis, and ultrafiltration) utilize the difference in the membrane permeability of molecules as a basis for separation. In dialysis, the flux of solutes across a membrane is mainly controlled by diffusional transport. Large surface area membrane modules such as hollow fiber units (Mahon and Lipps, 1971; Breslau et al., 1975; Stevenson et al., 1975; and Viswanadhan and Kramer, 1975) are often used to compensate for the slow diffusion-controlled flux. Hollow fiber dialysis has been successfully used, for example, in artificial kidney hemodialysis (Babb et al., 1971) to remove membrane-permeable waste materials from the blood. The application of dialysis so far has been limited to the separation of highly permeable solutes from practically impermeable colloids and particulates because of the low solute selectivity of currently available membranes. It is very difficult to obtain an appreciable degree of separation of solutes by dialysis if the permeabilities of the solutes are relatively close.

A single separation unit often achieves only a limited degree of separation. In order to obtain a desired degree of separation, the units are usually cascaded to construct a multistaged unit which multiplies the separation effect of each stage. This technique to enhance the separation is used for many separation processes. Gas phase multistaged separations which exploit the kinetic properties of gases as a basis for separation, e.g., mass diffusion (Maier, 1939), thermal diffusion (Clausius and Dickel, 1939), and gaseous diffusion (Hertz, 1922), have been known for many years. These operations are often used for the separation of isotopes. In aqueous systems, Ohya and Sourirajan (1969) and Kimura et al. (1969) proposed a multistaged reverse osmosis process for the separation of solutes from solution. Dialysis, on the other hand, has been almost exclusively used as a single-staged operation for the separation of highly permeable solutes from impermeable solutes. This investigation extends the possible application of dialysis to the fractionation of solutes having similar permeabilities.

## CONCLUSIONS AND SIGNIFICANCE

Continuous dialysis separation of solutes having similar membrane permeabilities can be achieved by a multistaged cascade operation of dialyzers coupled with several concentrators. The degree of solute separation is not increased by a multistaged continuous dialysis without a concentrator. Large numbers of concentrators are often required to achieve the desired degree of the separation of solutes if a conventional

counter-current cascade configuration of concentrator-dialyzer pairs is used. In this report, a novel cascade configuration which requires fewer concentrators to obtain the same degree of separation is presented. The successful development of a scheme to reduce the requirement of the number of concentrators is rather important since the concentrators usually contribute greatly to the cost of the solute separation. The results of the analysis of the multistaged dialysis systems are given in the form of a McCabe-Thiele diagram. The feasibility of separating solutes having relatively similar permeabilities is shown.

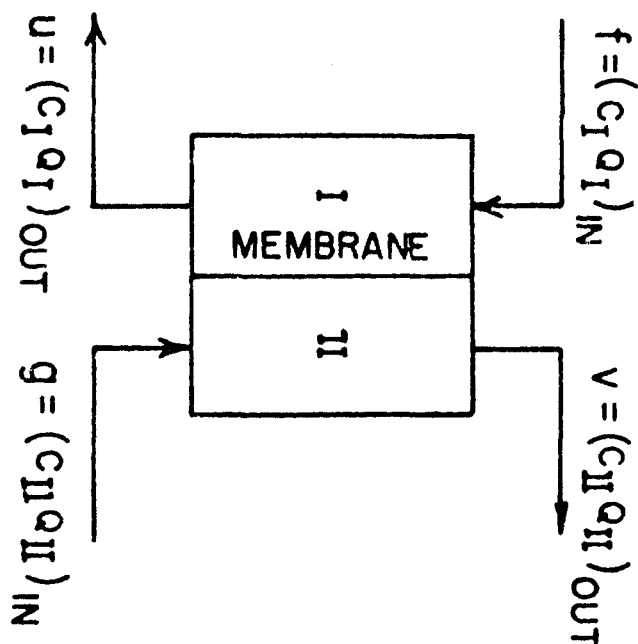


Figure 1. Schematic representation of a counter-current membrane mass exchanger. Volumetric flow rates of the two streams are identical in magnitude but opposite in flow direction.

## ANALYSIS

### Single Dialyzer

Consider a simple counter-current membrane mass exchanger (Figure 1): the two streams of solutions are separated by a permeable membrane of effective surface area  $S$ ; and solutes can be transferred by diffusion from one stream to the other. A well-packed hollow fiber dialyzer, for example, may be considered a mass exchanger of this type. The bulk solute concentrations,  $C_I$  and  $C_{II}$ , of the two solutions are functions of the distance from the entry points of the solutions to the dialyzer. The feed molar flow rates,  $f$  and  $g$ , and the product molar flow rates,  $u$  and  $v$ , are given by:

$$f = (C_I Q_I)_{in} \quad (1)$$

$$g = (C_{II} Q_{II})_{in} \quad (2)$$

$$u = (C_I Q_I)_{out} \quad (3)$$

$$v = (C_{II} Q_{II})_{out} \quad (4)$$

If the magnitudes of the volumetric flow rates,  $Q_I$  and  $Q_{II}$ , of the two solution streams are identical to one another:

$$Q_I = Q_{II} = Q \quad (5)$$

the steady state component balance of a solute will be given by:

$$u = (1 - E)f + Eg \quad (6)$$

$$v = Ef + (1 - E)g \quad (7)$$

The dimensionless number  $E$  is the *fractional extraction* of the solute, i.e., the fraction of solute molecules transferred from one solution stream to the other during dialysis operation. In the present discussion, the term *single dialyzer* refers to this counter-current membrane mass exchanger operated with two solution streams having the same magnitude of volumetric flow rate.

Michaels (1966) has shown that the fractional extraction of a single dialyzer can be expressed in a very simple form:

$$E = \frac{\theta}{1 + \theta} \quad (8)$$

The dimensionless *dialysis coefficient*  $\theta$  is given by:

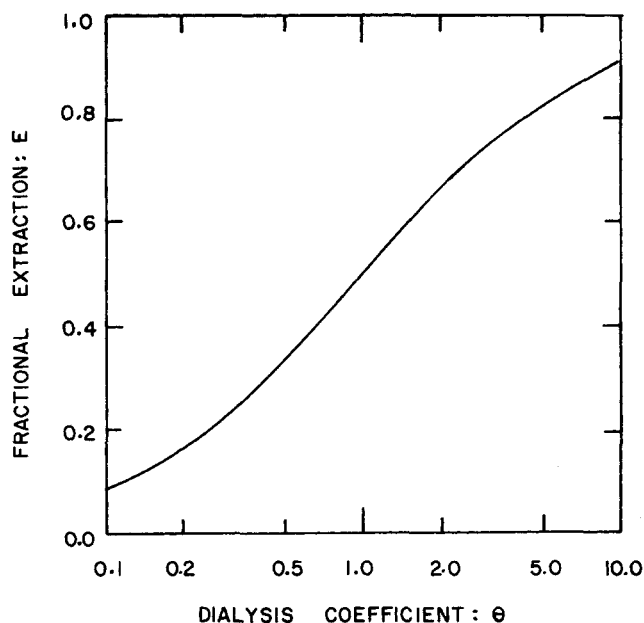


Figure 2. Fractional extraction of a single dialyzer as a function of dialysis coefficient.

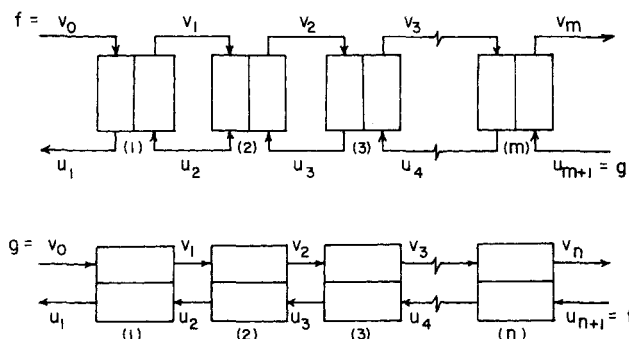


Figure 3. Simple counter-current cascades of dialyzers: parallel configuration (top) and series configuration (bottom).

$$\theta = \frac{hS}{Q} \quad (9)$$

where  $h$  is the overall mass transfer coefficient of a solute in the single dialyzer. If the mass transfer resistance of the solute in the membrane is much higher than that in the solution phase, the overall mass transfer coefficient can be approximated by the *membrane permeability*. The values for the permeabilities of solutes have been reported by various investigators (Colton et al., 1971; Klein, 1976). Detailed theoretical analysis of mass transfer in a hollow fiber dialyzer is given by Noda and Gryte (1978). The experimental studies of well-packed counter-current hollow fiber dialyzers (Noda et al., 1980) confirms the validity of Eqs. 7, 8 and 9. The fractional extraction  $E$  for a single dialyzer is plotted in Figure 2 as a function of  $\theta$ .

If a solution mixture containing two different solutes is dialyzed, the fractional extraction for each solute can be estimated from the individual membrane permeability, which determines the dialysis coefficient of the solute. The difference between the fractional extractions of the two solutes is equivalent to the *extent of separation*, a generalized separation index introduced by Rony (1972), between the two solutes. Figure 2 shows that the fractional extraction for a single dialyzer is not strongly affected by the change in dialysis coefficient. For example, even if the two solutes in a solution mixture to be dialyzed have the membrane permeability ratio of 100:1, the corresponding ratio of fractional extractions will be at most

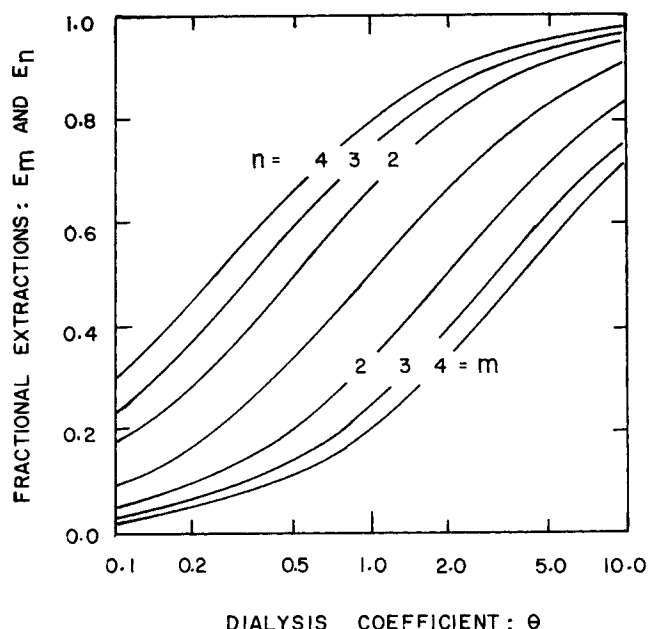


Figure 4. Fractional extractions of simple counter-current cascades as functions of dialysis coefficient and order of cascade.

10:1. The efficiency of a single dialyzer to fractionate solutes is, therefore, very low unless the permeability difference between the solutes is extremely large.

#### Counter-Current Cascade of Single Dialyzers

It is common in separation processes to develop a multistaged unit when a single-staged unit fails to achieve the desired degree of separation. In a multistaged system, units are repeated to multiply the effect of the separation. The schemes shown in Figure 3 are the familiar *counter-current cascade* configurations used in various equilibrium controlled separation processes such as liquid-liquid extraction and distillation. The steady-state input-output responses of these simple counter-current cascades of dialyzers are easily calculated.

The input-output response for  $k$ -th single dialyzer in the counter-current cascade of Figure 3(a) is:

$$u_k = \frac{1}{1 + \theta_k} v_{k-1} + \frac{\theta_k}{1 + \theta_k} u_{k+1} \quad (10)$$

$$v_k = \frac{\theta_k}{1 + \theta_k} v_{k-1} + \frac{1}{1 + \theta_k} u_{k+1} \quad (11)$$

where  $\theta_k$  is the dialysis coefficient of the  $k$ -th dialyzer. The overall input-output response of this  $m$ -th order counter-current cascade of single dialyzers is expressed in the form:

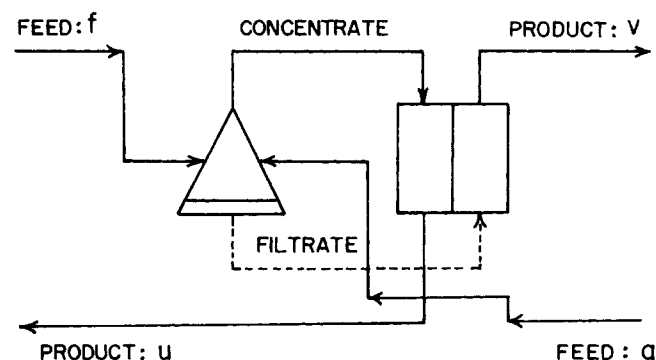


Figure 6. Concentrator-dialyzer pair (CDP).

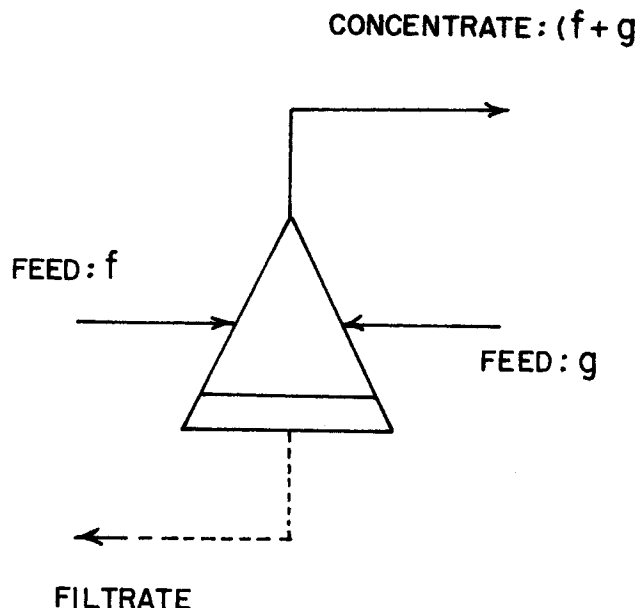


Figure 5. Nonselective concentrator. The broken line indicates the flow of stripped solvent.

$$u_1 = (1 - E_m)f + E_m g \quad (12)$$

$$v_m = E_m f + (1 - E_m)g \quad (13)$$

Solving Eqs. 10 and 11, the overall fractional extraction  $E_m$  of the cascade is obtained:

$$E_m = \frac{\left[ \sum_{k=1}^m \theta_k^{-1} \right]^{-1}}{1 + \left[ \sum_{k=1}^m \theta_k^{-1} \right]^{-1}} \quad (14)$$

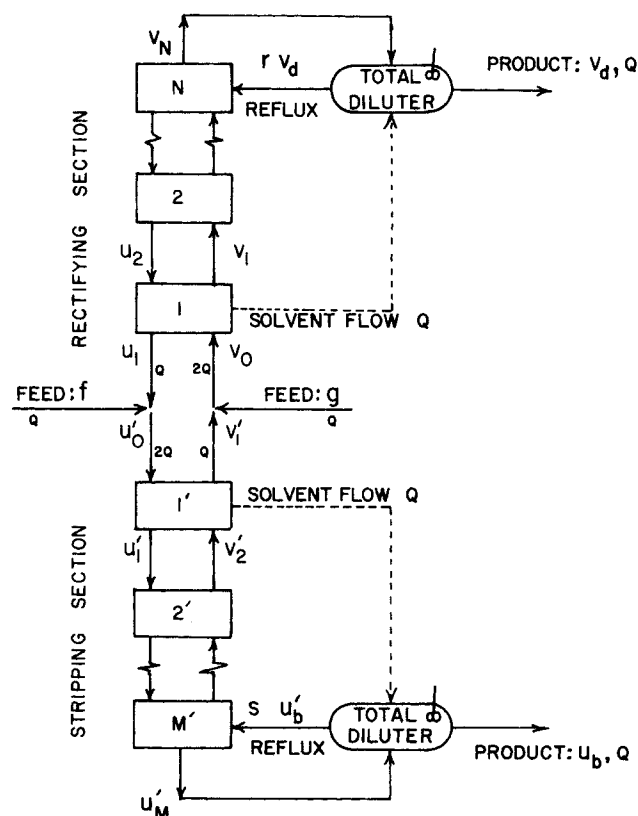


Figure 7. Counter-current cascade. Each stage corresponds to CDP (Figure 6) or DSA (Figure 9).

If the dialysis coefficient  $\theta_k$  is constant for all  $k$ , Eq. 14 simplifies to:

$$E_m = \frac{(\theta/m)}{1 + (\theta/m)} \quad (15)$$

It is possible to obtain a similar result by reducing the permeability of a single dialyzer by a factor of  $m$  by, for example, increasing the thickness of the membrane instead of cascading many single dialyzers. The overall input-output response of the other counter-current cascade of a single dialyzer (Figure 3b) is obtained in a similar manner. The input-output response of the  $k$ -th dialyzer is:

$$u_k = \frac{\theta_k}{1 + \theta_k} v_{k-1} + \frac{1}{1 + \theta_k} u_{k+1} \quad (16)$$

$$v_k = \frac{1}{1 + \theta_k} v_{k-1} + \frac{\theta_k}{1 + \theta_k} u_{k+1} \quad (17)$$

The form of the overall input-output response is the same as in Eqs. 12 and 13. Solving Eqs. 16 and 17, the overall fractional extraction  $E_n$  for this counter-current cascade of dialyzers becomes:

$$E_n = \frac{\sum_{k=1}^n \theta_k}{1 + \sum_{k=1}^n \theta_k} \quad (18)$$

For constant  $\theta_k$ , Eq. 18 simplifies to:

$$E_n = \frac{(n\theta)}{1 + (n\theta)} \quad (19)$$

It is possible to obtain the same result by, for example, increasing the surface area of the membrane in a single dialyzer.

The overall extractions  $E_m$  and  $E_n$  for the counter-current cascades of single dialyzers are plotted in Figure 4 as functions of the dialysis coefficient  $\theta$ . The value of  $\theta$  is assumed to be constant for all single dialyzers even though each dialyzer could be constructed with a different membrane surface area and thus has different  $\theta$ . Figure 4 shows that a simple counter-current cascade of dialyzers merely shifts the extraction curve around without increasing the selectivity of the dialysis unit.

### Concentrator-Dialyzer Pair (CDP)

Since a collection of dialyzers alone cannot increase the dialysis selectivity, a different type of separation unit is introduced. Figure 5 shows a *nonselective concentrator* which strips the solvent (water in aqueous systems) from a diluted feed solution while retaining most of the solutes in the concentrate solution. The broken line indicates the stream of stripped solvent. A reverse osmosis unit, for example, may be considered a solvent stripper if the solute of interest is excluded by the reverse osmosis membrane. The selection of the type of nonselective concentrator is not restricted to a reverse osmosis unit. For certain solutes, distillation, evaporation, or even freezing may be preferred to reverse osmosis. In general, these solvent strippers which may involve mechanical components such as high pressure pumps and flow controllers are much more expensive than the simple dialysis elements. A nonselective concentrator is coupled to a dialyzer in Figure 6. The input-output response of this *concentrator-dialyzer pair* (CDP) is:

$$u = \frac{1}{1 + \theta} (f + g) \quad (20)$$

$$v = \frac{\theta}{1 + \theta} (f + g) \quad (21)$$

The solute selectivity of a single dialyzer so far is not in-

creased by the introduction of a concentrator. However, using several units of CDP, a counter-current cascade dialysis system which greatly amplifies the selectivity of the dialyzers can be constructed (Figure 7). The *rectifying section* above the feed point has  $N$  stages, and the *stripping section* below the feed point has  $M$  stages. Each stage corresponds to a CDP in Fig. 6. The top stream having a solute molar flow rate  $v_N$  is divided into the product stream and the reflux stream. The ratio of the reflux molar flow rate to the overhead product molar flow rate  $v_d$  is the rectifying section reflux ratio  $r$ . The bottom stream  $u'_M$  is also divided into the reflux stream and the product stream. The ratio of the reflux molar flow rate to the bottom product molar flow rate  $u'_b$  is the stripping section reflux ratio  $s$ . Although the molar flow rates,  $u$  and  $v$ , of the solute change from stage to stage, the total volumetric flow rate  $Q$  is practically constant since the mole fraction of the carrier solvent is assumed to be always near unity.

From Eq. 21, the molar flow rates of a solute from the  $i$ -th stage of the rectifying section are related by:

$$v_i = \theta_i u_i \quad (22)$$

In addition, the stage-to-stage mass balance and the reflux condition for the rectifying section are given by:

$$v_{i-1} = u_i + v_d \quad (23)$$

$$v_N = (1 + r)v_d \quad (24)$$

Assuming the value of  $\theta_i$  is constant for all  $i$ , Eqs. 22-24 are solved in terms of the overhead solute molar flow rate  $v_d$ . The solute molar flow rates,  $u_i$  and  $v_i$ , from the  $i$ -th stage in the rectifying section are:

$$u_i = \theta^{i-1-N} \left( 1 + r + \sum_{k=1}^{N-i} \theta^k \right) v_d \quad (25)$$

$$v_i = \theta^{i-N} \left( 1 + r + \sum_{k=1}^{N-i} \theta^k \right) v_d \quad (26)$$

At the bottom of the rectifying section, Eqs. 25 and 26 reduce to:

$$u_1 = \theta^{-N} \left( 1 + r + \sum_{k=1}^{N-1} \theta^k \right) v_d \quad (27)$$

$$v_o = \theta^{-N} \left( 1 + r + \sum_{k=1}^N \theta^k \right) v_d \quad (28)$$

In a similar manner, the molar flow rates,  $u'_j$  and  $v'_j$ , of a solute (primed notations indicate the stripping section) from the  $j$ -th stage are obtained. The input-output response of a CDP (Eq. 21), the stage-to-stage mass balance, and the reflux condition for the stripping section are given by:

$$v'_j = \theta'_j u'_j \quad (29)$$

$$u'_{j-1} - v'_j = u'_b \quad (30)$$

$$u'_M = (1 + s)u'_b \quad (31)$$

Again, the dialysis coefficient  $\theta'_j$  is assumed to be constant for the sake of mathematical simplicity. Solving Eqs. 29-31 in terms of the bottom product molar flow rate  $u'_b$ , the molar flow rates,  $u'_j$  and  $v'_j$ , from the  $j$ -th stage in the stripping section become:

$$u'_j = \theta^{M-j} \left( 1 + s + \sum_{k=1}^{M-j} \theta^{-k} \right) u'_b \quad (32)$$

$$v'_j = \theta^{M+1-j} \left( 1 + s + \sum_{k=1}^{M-j} \theta^{-k} \right) u'_b \quad (33)$$

At the top of the stripping section, Eqs. 32 and 33 reduce to:

$$u'_o = \theta^M \left( 1 + s + \sum_{k=1}^M \theta^{-k} \right) u'_b \quad (34)$$

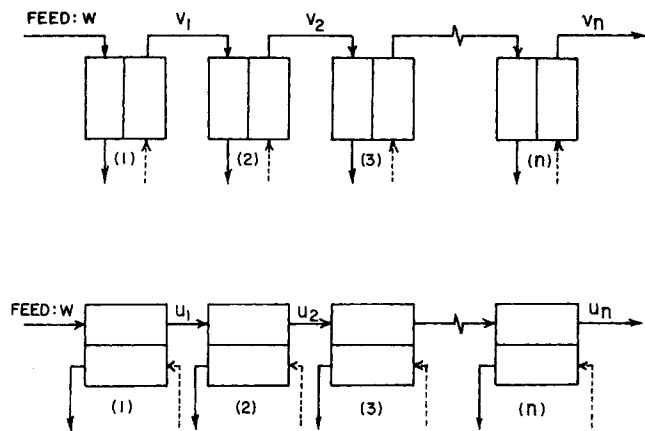


Figure 8. Cross-current cascades of dialyzers: parallel configuration (top) and series configuration (bottom). Broken lines indicate the flow of solvent free of the solute of interest.

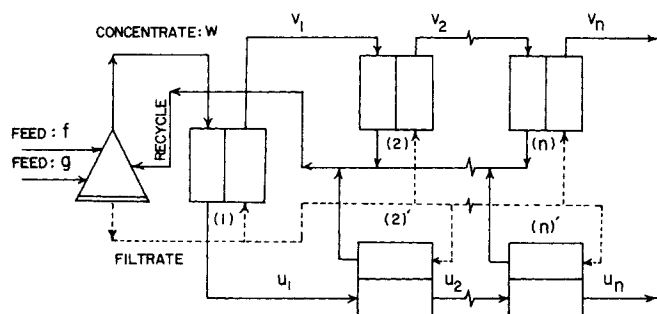


Figure 9. Dialysis selectivity amplifier (DSA).

$$v'_1 = \theta^M \left( 1 + s + \sum_{k=1}^{M-1} \theta^{-k} \right) u'_b \quad (35)$$

The mass balance at the feed point is given by:

$$u'_b = u_1 + f \quad (36)$$

$$v'_1 = v'_1 + g \quad (37)$$

Solving Eqs. 27, 28 and 34-37 simultaneously, the overall input-output response of the multistaged counter-current cascade of CDP is obtained:

$$u'_b = \frac{\rho f + (\rho - 1)g}{\rho + \sigma - 1} \quad (38)$$

$$v'_1 = \frac{(\sigma - 1)f + \sigma g}{\rho + \sigma - 1} \quad (39)$$

where

$$\rho = \theta^{-N} \left( 1 + r + \sum_{k=1}^N \theta^k \right) \quad (40)$$

$$\sigma = \theta^M \left( 1 + s + \sum_{k=1}^M \theta^{-k} \right) \quad (41)$$

When the counter-current cascade of CDP is operated under the condition of total reflux (i.e., the feed and the product molar flow rates,  $f$ ,  $g$ ,  $u_b$ , and  $v_d$ , are infinitely small compared with the internal molar flow rates,  $u_i$ ,  $v_i$ ,  $u'_j$ , and  $v'_j$ ), Eqs. 38 and 39 simplify to:

$$u'_b = \frac{1}{1 + \theta^{M+N}} (f + g) \quad (42)$$

$$v_d = \frac{\theta^{M+N}}{1 + \theta^{M+N}} (f + g) \quad (43)$$

### Dialysis Selectivity Amplifier (DSA)

The counter-current cascade (Figure 7) is found in many separation processes. For example, in gaseous diffusion (Hertz, 1922), compressors are used instead of solvent strippers, but the overall counter-current configuration is the same. A similar configuration has been proposed for a multistaged reverse osmosis (Ohya and Sourirajan, 1969; Kimura et al., 1969). This well-accepted cascade scheme, however, may not be the optimal configuration for dialysis systems. The large disparity in costs between a dialyzer and a solvent stripper such as a reverse osmosis unit suggests that a scheme which uses a small number of concentrators, even if it requires a large number of dialyzers, may be much more economical than a scheme which requires fewer dialyzers but a substantial number of concentrators. As shown in Figure 4, an assemblage of single dialyzers alone cannot amplify dialysis selectivity. By introducing only one concentrator, however, a totally new cascade configuration which improves the dialysis selectivity is developed.

Consider two sets of "n-th order" cross-current dialyzer cascades (Figure 8). Each cascade consists of  $n$  number of single dialyzers. The broken lines represent the flows not containing the solutes of interest. From Eqs. 5-8, the solute molar flow rates are given by:

$$u_i = \frac{1}{1 + \theta_i} u_{i-1} \quad (44)$$

$$v_j = \frac{1}{1 + \theta_j} v_{j-1} \quad (45)$$

If the dialysis coefficient  $\theta$  is constant for all the single dialyzers in the system, the output solute molar flow rates from the  $n$ -th dialyzers of the two cross-current cascades are given by:

$$u_n = \left( \frac{1}{1 + \theta} \right)^n w \quad (46)$$

and

$$v_n = \left( \frac{\theta}{1 + \theta} \right)^n w \quad (47)$$

where  $w$  is the input molar flow rate to both cascades.

These two  $n$ -th order cross-current cascades are now combined with a nonselective solvent stripper (Figure 9) to form a multistaged dialyzer network system: the *dialysis selectivity amplifier* (DSA). The feed and the recycle streams are directed to the concentrator; the resulting concentrate stream proceeds to the cross-current cascade sections; and the successive dialysis is carried out in the cascades with the solute free filtrate from the concentrator. The first single dialyzer is common to the two internal cross-current cascade sections. The total number of single dialyzers in a DSA is, therefore, given by  $2n - 1$ . The number  $n$  is the order of cascade of the DSA. From the overall mass balance, the total input and output molar flow rates of a solute are related by:

$$f + g = u_n + v_n \quad (48)$$

Combining Eqs. 46-48, the molar flow rate  $w$  of the concentrate stream from the concentrator becomes:

$$w = \frac{(1 + \theta)^n}{1 + \theta^n} (f + g) \quad (49)$$

The overall input-output response is obtained by substituting Eq. 49 into Eqs. 46 and 47:

$$u_n = \frac{1}{1 + \theta^n} (f + g) \quad (50)$$

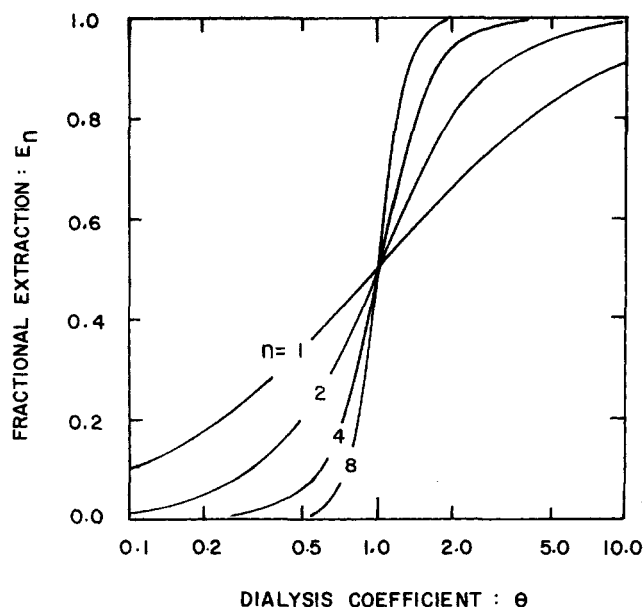


Figure 10. Fractional extraction of DSA as a function of dialysis coefficient and order of cascade.

$$v_n = \frac{\theta^n}{1 + \theta^n} (f + g) \quad (51)$$

The fractional extraction  $E_n$  of the  $n$ -th order DSA is:

$$E_n = \frac{\theta^n}{1 + \theta^n} \quad (52)$$

Note the similarity between the input-output response for the counter-current cascade of CDP in Figure 7 operated under the condition of total reflux (Eqs. 42 and 43) and that for DSA in Figure 9 constructed with only one concentrator (Eqs. 50 and 51). The counter-current cascade of CDP which requires many concentrators may achieve a separation identical to that of DSA by operating under conditions of total reflux. DSA, however, requires no additional reflux of the product streams to attain the same result. Thus, the two systems differ in the requirement of reflux as well as in the number of concentrators.

The extraction curves of DSA plotted as functions of  $\theta$  in Figure 10 pivot at the point where  $E_n = 0.5$  and  $\theta = 1$ . The dialysis selectivity is amplified along with the increase of the order of cascade for the system, i.e., the number of dialyzers in each internal cross-current cascade section of the DSA. As the order of cascade for DSA increases to a very large number, the system gives an almost discrete input-output response: all the solutes which have a value of  $\theta$  greater than unity will be found in the upper product stream; the rest of the solutes will come out in the lower stream. Thus, complete separation of the solutes having similar permeabilities is expected.

The number of dialyzers in DSA, however, cannot be increased indiscriminately because of a serious operational difficulty. When the order of cascade for DSA is very high, the total flow rate of the recycle streams from the  $(2n - 1)$  dialyzers becomes so immense that the concentrator will simply be overloaded. The increase in the recycle results not only in an increase of the volume of the solution entering the concentrator, but also in an accumulation of solutes at high concentration in the concentrator output stream. From Eq. 47, this accumulation of solutes is expressed as the ratio of the molar flow rate of the concentrate stream to that of the feed stream:

$$\frac{w}{f + g} = \frac{(1 + \theta)^n}{1 + \theta^n} \quad (53)$$

A plot of this solute accumulation ratio in Figure 11 shows that the maximum accumulation ratio of  $2^{n-1}$  is expected for a solute

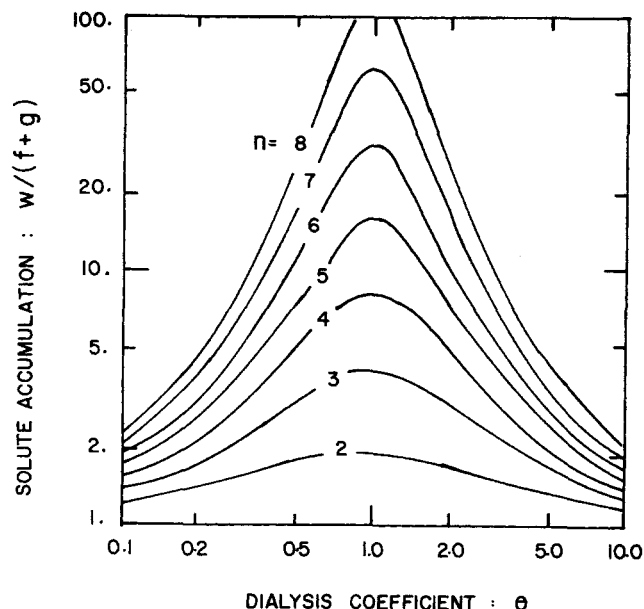


Figure 11. Solute accumulation in DSA as a function of dialysis coefficient and order of cascade.

having a dialysis coefficient  $\theta$  of unity. As the order of cascade for DSA increases, the accumulation becomes so large that solute precipitation, gelation, or significant increase in solution osmotic pressure may occur; and a strong deviation in the input-output response of the dialyzers from the predictions based on a dilute system will be expected. In short, the entire system collapses unless the feed solutions are very dilute.

#### Counter-Current Cascade of DSA

The solute accumulation problem sets a practical upper limit on the number of single dialyzers in DSA. Since the order of cascade for DSA cannot be increased indiscriminately, there will be a limit to the degree of separation which a single DSA can achieve. On the other hand, the counter-current cascade of CDP shown in Figure 7 does not have this solute accumulation problem. The order of counter-current cascade can be increased sufficiently to yield a high degree of separation. The CDP counter-current cascade, however, requires many concentrators and a large reflux of the product streams, while DSA is constructed with only one concentrator. In order to complement the shortcomings of each system, a hybrid configuration between the two (i.e., the counter-current cascade of DSA) is considered.

Compare the input-output response of a CDP (Figure 6) given in Eqs. 20 and 21 to that of a DSA (Figure 9) given in Eqs. 50 and 51. The only difference between the two is that the dialysis coefficient  $\theta$  is raised to the  $n$ -th power in the latter unit. The configuration of DSA of the first order cascade is identical to that of CDP. The CDP can, therefore, be treated as a special form of DSA. Suppose the basic first order DSA (i.e., CDP) in the counter-current dialysis cascade (Figure 7) is replaced by the  $n$ -th order DSA. The overall input-output response of this cascade becomes identical to Eqs. 38 and 39 except that the dialysis coefficient  $\theta$  in Eqs. 40 and 41 is replaced by  $\theta^n$ . Even though the number of concentrators in the cascade is not changed by this replacement, the selectivity of the system is greatly improved: the number of concentrators required to achieve a desired degree of separation is drastically reduced by using DSA instead of CDP.

#### RESULTS

##### McCabe-Thiele Diagram

The performance of a multistaged separation process for a binary mixture is often summarized in the form of the

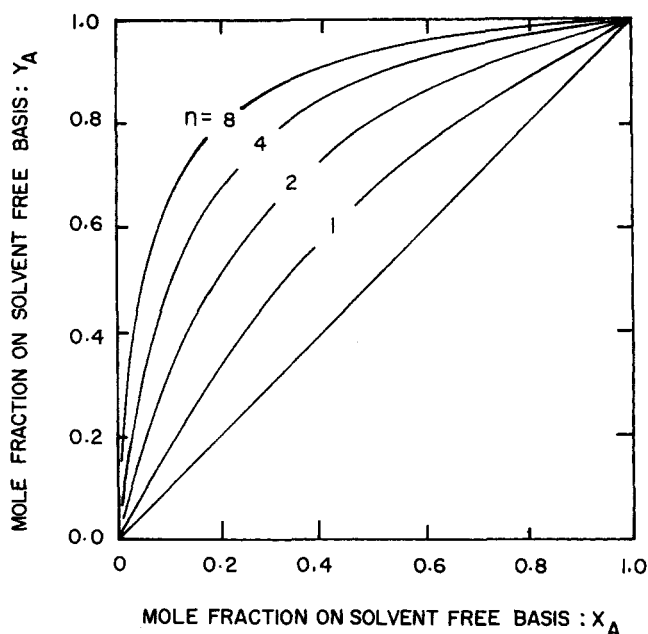


Figure 12. Extraction curves of DSA for various orders of cascade. Relative permeability is 2.0.

McCabe-Thiele diagram. In order to construct this diagram for a dialysis system, the concepts of *relative permeability* and solute mole fraction on a *solvent free basis* are introduced. Suppose a feed solution containing two types of solutes, A and B, in a carrier solvent is fed to a CDP. The separation factor in a dialysis system is given by the relative permeability  $\alpha_{AB}$  which is defined as:

$$\alpha_{AB} = \frac{h_A}{h_B} \quad (54)$$

By convention, solute A is more permeable than solute B. From Eq. 7, the relative permeability is also given by the ratio of the dialysis coefficients:

$$\alpha_{AB} = \frac{\theta_A}{\theta_B} \quad (55)$$

The mole fraction of A and B in the product stream on a solvent-free basis are given:

$$x_A = \frac{u_A}{u_A + u_B} \quad (56)$$

$$x_B = 1 - x_A \quad (57)$$

$$y_A = \frac{v_B}{v_A + v_B} \quad (58)$$

$$y_B = 1 - y_A \quad (59)$$

Since the solute molar flow rates in the product streams of CDP are related by Eqs. 21 and 22, Eqs. 57-59 yield:

$$x_A = \theta_A y_A \quad (60)$$

$$(1 - x_A) = \theta_B (1 - y_A) \quad (61)$$

The combination of Eqs. 62 and 63 gives:

$$\frac{y_A(1 - x_A)}{x_A(1 - y_A)} = \frac{\theta_A}{\theta_B} \quad (62)$$

Since this ratio of the dialysis coefficients is simply the relative permeability  $\alpha_{AB}$  (Eq. 55), the extraction curve equation of the McCabe-Thiele diagram for CDP is obtained in terms of  $\alpha_{AB}$ .

$$y_A = \frac{\alpha_{AB} x_A}{1 + \alpha_{AB} x_A - x_A} \quad (63)$$

The equation for the extraction curve in the McCabe-Thiele diagram is also obtained for the  $n$ -th order DSA. The input-output response of the unit is identical to that of a CDP except that the dialysis coefficient is raised to the  $n$ -th power. Therefore, the extraction curve equation for DSA becomes:

$$y_A = \frac{(\alpha_{AB})^n x_A}{1 + (\alpha_{AB})^n x_A - x_A} \quad (64)$$

Figure 12 shows the set of extraction curves for various cascade orders at  $\alpha_{AB} = 2$ . The increase of the order of DSA shifts the extraction curve away from the  $y_A = x_A$  line of the McCabe-Thiele diagram. The shift is equivalent to an increase in the relative permeability.

The McCabe-Thiele diagram in Figure 13 shows the separation of a solute A by the counter-current cascade of CDP. The composition of streams from each stage is calculated from Eqs. 25, 26, 32, and 33. The feed composition of 40% A on a solvent free basis and a relative permeability  $\alpha_{AB}$  of 2.0 are chosen. The stage-to-stage calculation shows that a purity of 95% A is achieved in the overhead stream with sixteen stages. The required reflux ratios,  $r$  and  $s$ , are 0.9 and 0.7, respectively. Given the volumetric flow rate  $Q$  of the solution stream in each dialyzer, the total filtration rate of the concentrator becomes  $18Q$ :  $Q$  for each CDP and additional  $2Q$  for each of the feed points. On the other hand, when the fourth order DSA is used in the counter-current cascade, the McCabe-Thiele diagram for the same feed conditions becomes Figure 14. Only four stages of DSA are required to produce the overhead product stream with a composition of 98% A on a solvent free basis. Moreover, the reflux ratios,  $r$  and  $s$ , in this case are both zero, i.e., no reflux of the product stream is required to achieve the degree of separation. Under zero reflux conditions, only the solvent (water) is supplied at the top and bottom stages of the counter-current cascade. The total filtration rate within the concentrators of the cascade is  $28Q$ :  $7Q$  for each fourth order DSA except for the top and bottom units;  $6Q$  for the top and bottom stages because of the zero reflux conditions; and  $2Q$  for the feed points.

The number of stages required for a given degree of separation becomes minimum when the counter-current cascade is operated under the condition of total reflux. Since the relative permeability  $\alpha_{AB}$  is constant for all the stages, the minimum number of stages  $N_{\min}$  for the counter-current cascade of the  $n$ -th order DSA is given by the Fenske (1932) equation:

$$N_{\min} = \frac{1}{n} \frac{\log \left[ \frac{y_{dA}(1 - x_{dA})}{x_{bA}(1 - y_{bA})} \right]}{\log \alpha_{AB}} \quad (67)$$

The minimum number of stages  $N_{\min}$  is inversely proportional to the order  $n$  of DSA.

### Economic Evaluation

Suppose the four-stage counter-current cascade of fourth order DSA is constructed to obtain the degree of separation predicted by the McCabe-Thiele diagram in Figure 14. Only four nonselective concentrators are required to reconcentrate the recycle solutions from 28 dialyzers. It is assumed that reverse osmosis is the method used for this concentration step. In order to circulate the solution streams through each dialyzer in the system, only one multichannel peristaltic pump is required. On the other hand, four separate high pressure pumps must be used to reconcentrate the solution by reverse osmosis. Each reverse osmosis unit uses a semi-permeable membrane the total surface area of which is comparable to that of a dialyzer. The major fraction of the capital cost for the process lies in the solution reconcentration steps.

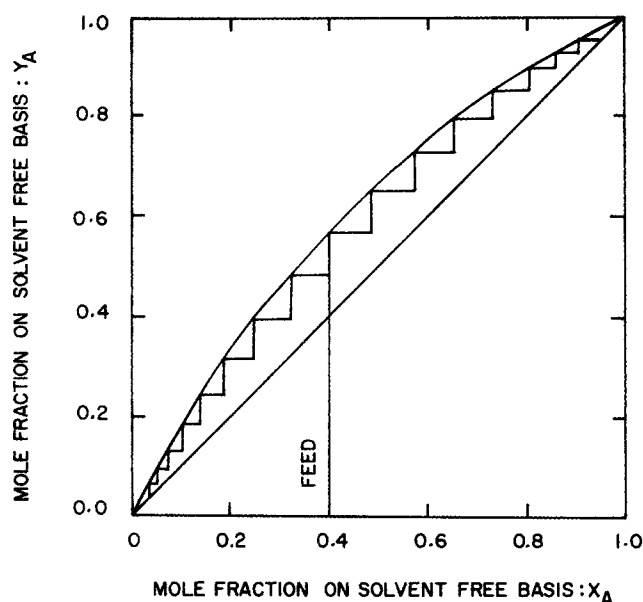


Figure 13. McCabe-Thiele diagram for a counter-current cascade of CDP.

A dialyzer (10 cm in diameter and 100 cm long) containing  $10^5$  hollow fibers (0.03 cm in diameter) may have a total membrane surface area of  $10^6 \text{ cm}^2$ . For typical middle molecule solutes having permeabilities in the range of  $10^{-4} \text{ cm/s}$ , this dialyzer can be operated with a volumetric flow rate of about  $100 \text{ cm}^3/\text{s}$ . If the volumetric flow rate of the feed to the cascade of DSA is also  $100 \text{ cm}^3/\text{s}$ , each reverse osmosis unit in a fourth order DSA has to filter the combined feed and recycle stream at a rate of about  $700 \text{ cm}^3/\text{s}$ . Typically, the operational characteristics of a reverse osmosis separation unit might be: total daily flux  $60 \text{ m}^3$ ; membrane permeability  $7.1 \times 10^{-4} \text{ cm/s}$ ; membrane area  $99 \text{ m}^2$ . For such a system, Klinkowski (1978) and Kirjassoff, Pinto and Hoffman (1980) project a capital cost of \$30,000 and an operational cost of \$1.32/ $\text{m}^3$  for each reverse osmosis unit. Four such RO units are required for this example. The cascade of CDP represented by the McCabe-Thiele diagram in Figure 13 requires twelve more reverse osmosis units than the cascade of DSA to achieve the same separation.

## DISCUSSION

In a large fluid flow system, the cumulative effect of the pressure drop in each element of the system may become important. For a typical well-packed hollow fiber dialyzer which is operated to fractionate solutes of middle molecule range with volumetric flow rate per fiber of  $10^{-3} \text{ cm}^3/\text{s}$ , the estimated pressure drop between the entrance and exit points of a hollow fiber (0.03 cm diameter and 100 cm long) is about  $5 \times 10^4 \text{ dynes/cm}^2$ ; the pressure drop is relatively small. The pressure drop outside the hollow fibers has comparable value to the small pressure drop inside the fibers when these hollow fibers are well packed in a dialyzer shell. The average trans-membrane pressure difference, therefore, is usually very small. The effect of osmotic pressure may become important if the concentration difference between the adjacent solutions in a dialyzer is large. The volumetric flux across the membrane driven by both hydraulic and osmotic pressure can be easily minimized by applying the back pressure to compensate the excess pressure.

The exact conservation of the volumetric flow rates of the solutions in a dialyzer is actually not very important if the input-output response of the dialyzer can be determined. The theoretical treatment of solute flux across a membrane accompanied by a volumetric flux is well developed (Kedem and Katchalsky, 1958). However, the mathematical expression for the prediction of the input-output response of a counter-current dialyzer becomes rather complex since at least two

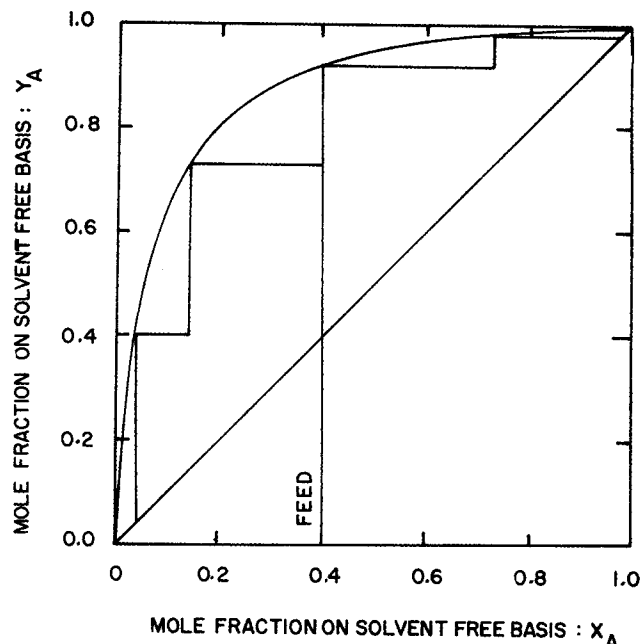


Figure 14. McCabe-Thiele diagram for a counter-current cascade of fourth order DSA.

additional parameters, hydraulic permeability and reflection coefficient, must be incorporated to account the effect of volumetric flux across the membrane.

In order to calculate the input-output response of a single dialyzer, various simplifying assumptions based on dilute solution systems are made: flux of solute is proportional to the concentration gradient (Fick's law); permeability is not a function of solute concentration; and interactions between solutes are negligible. Again, these conditions are not essential for the dialysis separation of solutes but useful for the development of a simple mathematical expression to describe the multistaged dialysis systems. If a better expression for a single dialyzer input-output response is obtained, the prediction of the behavior of the multistaged system can be further improved. One of the most important physical requirements for the successful construction of multistaged dialysis system is that solute can be separated from solvent by a nonselective concentrator. In practice, the complete separation of solvent is rarely achieved. The incomplete separation of leaky solutes may cause a change in the overall input-output response. This effect is not included in the present investigation.

## NOTATION

$C$	= concentration of solute ( $\text{mol}/\text{cm}^3$ )
$E$	= fractional extraction of a single dialyzer
$E_n$	= fractional extraction of an $n$ -th order DSA
$M$	= number of stages in the stripping section of a counter-current cascade of CDP or DSA
$N$	= number of stages in the rectifying section of a counter-current cascade of CDP or DSA
$N_{\min}$	= minimum number of stages required
$Q$	= volumetric flow rate ( $\text{cm}^3/\text{s}$ )
$S$	= surface area of a membrane in a single dialyzer ( $\text{cm}^2$ )
$f$	= molar flow rate of a solute in the feed ( $\text{mol}/\text{s}$ )
$g$	= molar flow rate of a solute in the feed ( $\text{mol}/\text{s}$ )
$h$	= permeability of a solute ( $\text{cm}/\text{s}$ )
$n$	= order of cascade for DSA
$r$	= reflux ratio in the rectifying section
$s$	= reflux ratio in the stripping section
$u$	= molar flow rate of a solute in product ( $\text{mol}/\text{s}$ )
$v$	= molar flow rate of a solute in product ( $\text{mol}/\text{s}$ )
$w$	= molar flow rate of a solute in the concentrate ( $\text{mol}/\text{s}$ )
$x$	= mole fraction on solvent free basis
$y$	= mole fraction on solvent free basis



## Greek Letters

$\alpha$	= relative permeability
$\theta$	= dialysis coefficient defined in Eq. 9
$\rho$	= defined in Eq. 40
$\sigma$	= defined in Eq. 41

## Subscripts

A	= more permeable solute
B	= less permeable solute
I	= region in a dialyzer
II	= region in a dialyzer
b	= bottom
d	= overhead

## Abbreviations

CDP	= concentrator-dialyzer pair (Figure 6)
DSA	= dialysis selectivity amplifier (Figure 9)

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# Modeling the Flow of Viscoelastic Fluids Through Porous Media

A tube with sinusoidal axial variations in diameter has been used as a first step toward modeling the flow channels of a porous medium in such a way that appreciable Lagrangian unsteadiness is present. Experiments with dilute aqueous solutions of a polyacrylamide (Dow Separan AP-30) show that the Lagrangian unsteadiness gives rise to an increase in resistance to flow through the sinusoidal channel relative to that predicted for a purely viscous fluid. The increase in pressure drop can occur as a consequence of fluid elasticity, without any observable secondary flow. At sufficiently high flow rates, secondary flow appears.

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## SCOPE

In a recent paper (Deiber and Schowalter, 1979) we showed how a technique of geometric iteration could be used to obtain solutions to the Navier-Stokes equation for flow through tubes with sinusoidal axial variations in diameter, where the amplitude of variation is comparable to the average radius. In the present work this technique is extended to flow of viscoelas-

tic fluids. The theoretical results are accompanied by data on pressure drop and streamline profiles for dilute aqueous solutions of polyacrylamide (Dow Separan AP-30).

The research was motivated by a desire to model the flow of viscoelastic liquids through porous materials by means of a geometry sufficiently realistic to include the most important aspects of the flow, but sufficiently simple to be mathematically tractable. We believe that the sinusoidal geometry is an effec-

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