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ASYMMETRIC PERMEATORS - A CONCEPTUAL STUDY

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ABSTRACT

The asymmetric permeator concept of Ohno et. al. utilizing two different membranes for rare gas separation has been explored in general. Various geometrical arrangements and possible applications to gas separations other than rare gas-nitrogen mixtures have been discussed. The utility of an asymmetric permeator for multicomponent gas separations has been investigated. The separation factor of a ternary system in a perfectly mixed asymmetric permeator has been obtained. The amount of separation obtained with a ternary feed in a perfect crossflow stage having no axial mixing has been analytically determined for some limiting cases with an asymmetric permeator. The asymmetric permeator concept has been extended also to a high separation factor liquid solution separation process like reverse osmosis desalination. Preliminary calculations have been carried out to show that an asymmetric desalinator with reverse osmosis (RO) and piezodialysis (PD) membranes has a lower increase in brine concentration along the module length for a given water recovery resulting in a lower operating pressure. With hollow fiber asymmetric desalinators having RO and PD membranes, the concentration polarization, if any, may be significantly reduced. Practical applications of asymmetric permeators for phenol-water separation etc. have been discussed.

INTRODUCTION

Membrane separation processes utilize at present a single type of membrane and are therefore capable of only binary separ-

ations due to the existence of discontinuous chemical potential profile at the membrane surface (1). Multicomponent separations are possible in a membrane separator only if at least two different types of membranes are utilized simultaneously. Each such membrane should preferentially separate one chemical species instead of just one ionic species as is true in a cell pair of an electrodialysis unit having a cation exchange and an anion exchange membrane. Membrane separators having two different types of membranes capable of different separations are termed asymmetric permeators. The only example of an asymmetric permeator although applied to a binary separation, is available in the investigations by Kimura, Nomura, Miyauchi and Ohno (2). Ohno and coworkers had separated a N_2-Kr mixture (3) by using a separation cell with both cellulose acetate and silicone rubber membranes. While krypton has higher permeability than nitrogen through a silicone rubber membrane, nitrogen has a higher permeability than krypton through a cellulose acetate membrane. Ohno et. al. (3) have thereby shown that the binary separation factor in such an asymmetric gas permeator is greater than that obtainable in a separator with a single type of membrane. Such an asymmetric permeator, then, like the continuous membrane column of Hwang and Thorman (4), is an improvement over a conventional single stage membrane separator with a not-too-large separation factor for binary gas separations.

This paper deals with a conceptual study of the asymmetric permeator in general. The asymmetric separator concept is extended here to various gas and liquid separations with existing and/or improved versions of membranes (likely to be available in future). Multicomponent gas separations by asymmetric permeators have been considered. The separation factor expressions for a ternary gas mixture in a perfectly mixed asymmetric permeator have been studied. The stage analysis for a perfect crossflow pattern has also been carried out for some limiting cases with a ternary gas system. Although the asymmetric per-

meator concept is useful for separations with not-too-large separation factors, it has been extended to a large separation factor process, reverse osmosis desalination. The possible advantages of carrying out desalination in an asymmetric permeator with reverse osmosis and piezodialysis membranes have been explored with regard to a reduction in high pressure feed brine concentration along the permeator as well as concentration polarization. The utility of such separators for other liquid solutions have also been considered.

DESCRIPTION OF ASYMMETRIC PERMEATORS

The schematic description of an asymmetric permeator with two different membranes, as available in Ohno et.al. (3), is shown in Figure 1. The high pressure side output stream with dotted lines is absent in Ohno et. al. (3) scheme. Therefore, the asymmetric permeator of Figure 1 with three output streams is different from an asymmetric separator in which there are only two output streams and the heads separation factor is different from the tails separation factor. The practical

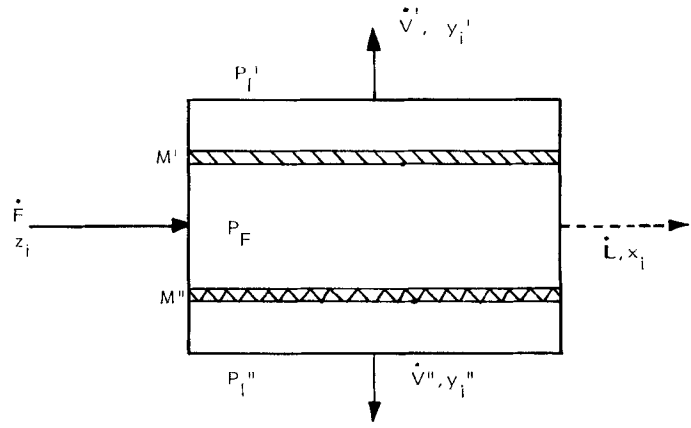

FIGURE 1. ASYMMETRIC PERMEATOR-SCHEMATIC

arrangement of the asymmetric permeator in Ohno et. al. (3) consists of membrane capillaries of dimensions around 1 mm O.D. and 0.5 mm I.D. bundled together with both ends opening to a chamber through a tube sheet in a shell and tube configuration. Different membranes are connected to the opposite tube sheets in a configuration shown schematically in Figure 2, which also has a shell side outlet absent in the scheme of Ohno et. al. (3). For different applications, one could use hollow fibers instead of capillaries. For hollow fiber configurations, if it is desired that the different membranes should be kept evenly dispersed amongst each other instead of each type being bundled separately, one could make the lengths of the hollow fibers of one material such that they get sealed in the tube sheet meant for the other membrane material. Thus, hollow fibers of one material will discharge at one end of the permeator through their own tube sheet while at the other end, they will be sealed in the tube sheet for the other material.

Another possible arrangement could be a stack of parallel membranes arranged in the manner of Figure 3 with suitable spacers

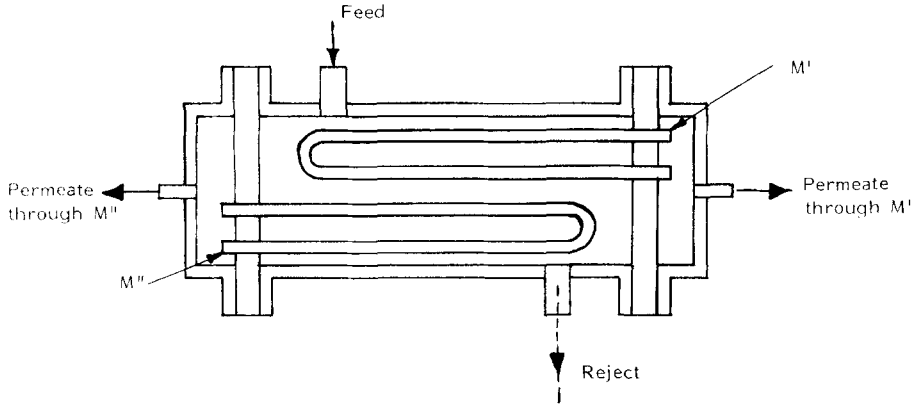

FIGURE 2. ASYMMETRIC PERMEATOR-SCHEMATIC WITH HOLLOW FIBER MEMBRANES

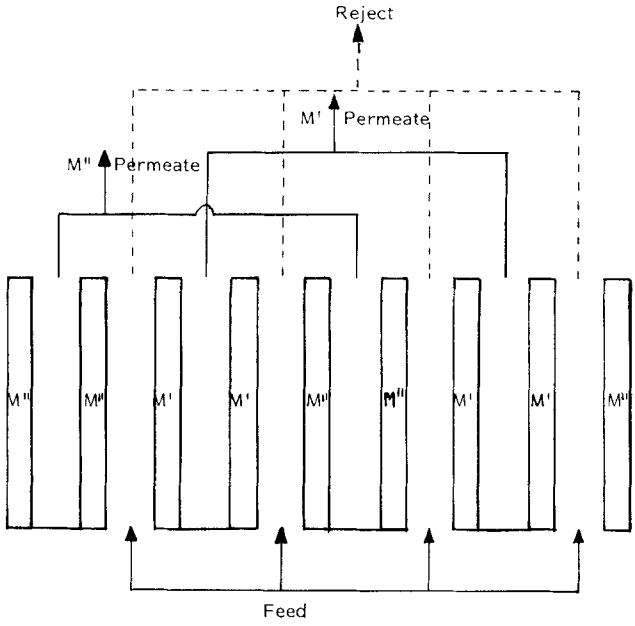

FIGURE 3. ASYMMETRIC PERMEATOR-SCHEMATIC WITH FLAT MEMBRANES

in between to provide chambers. Those chambers with different membranes M' and M" on two sides will be open to the feed gas mixture inside a pressure vessel containing the stack. The chambers with similar membranes on both sides will be the permeate chambers with connections to similar chambers through a distributor at the ends. With two distributors, the two product streams can be taken out of the vessel without contaminating the products with the feed stream. For a liquid mixture, it is not necessary to have a shell and membrane stack arrangement. Rather, the arrangement commonly used in electrodialysis can be conveniently utilized eliminating the shell and feeding the feed chambers through another distributor. For gas separations, if a purge or sweep gas (or vapor) is necessary, an additional distributor may be used to feed the permeate collection chambers.

It should be pointed out that supporting the membranes against high feed pressure will be a problem in such an arrangement.

Asymmetric permeators with more than two different membranes are also possible. However, the practical design of such permeators will be quite difficult especially with flat membranes.

SEPARATION FACTOR IN A PERFECTLY MIXED ASYMMETRIC GAS PERMEATOR

We will treat the cases of binary and ternary separations for a gas mixture in a perfectly mixed asymmetric permeator. For a binary gas mixture, consider the separator shown in Figure 1. In the scheme of Ohno et. al. (3)(2), a binary gas mixture enters the permeator with a molar flow rate of $\dot{F}$ and a mole fraction z_1 of species 1. Through membranes M' and M", two fractions of gas with mole fractions y_1' and y_1'' are obtained respectively. Since there is no reject gas in Ohno et. al. (3)(2), $\dot{L} = o$. For a completely mixed stage, therefore, the high pressure side gas composition is everywhere z_1. If the pressures in the three regions are P_F, P_1' and P_1'' and the permeabilities of the species i through membranes M' and M" are respectively Pr_i' and Pr_i'' then, for simple gas permeation, it may be easily shown following Ohno et. al. (3) that the stage separation factor α_{12} between permeate streams having flow rates $\dot{V}'$ and $\dot{V}''$ is

$$\alpha_{12} = \frac{y_1'\ (1 - y_1'')}{(1 - y_1')\ y_1''} = \left[\frac{y_1'(1 - z_1)}{(1 - y_1')z_1}\right]\left[\frac{z_1\ (1 - y_1'')}{(1 - z_1)y_1''}\right] \qquad (1)$$

Since $y_1'\ \dot{V}' = Pr_1'\ A_M' \left[P_F\ z_1 - P_1'\ y_1'\right]$ (1a)

and $y_2'\ \dot{V}' = (1 - y_1')\ \dot{V}' = Pr_2'\ A_M' \left[P_F z_2 - P_1'\ y_2'\right]$ (1b)

and similarly for membrane M" where A_M' is the membrane area of M' (A_M'' for M" membrane), we obtain

$$\alpha_{12} = \alpha_{12}^{'*}\left[\frac{1 - \frac{P_1'}{P_F}\frac{y_1'}{z_1}}{1 - \frac{P_1'}{P_F}\frac{y_2'}{z_2}}\right]\frac{1}{\alpha_{12}^{"*}}\left[\frac{1 - \frac{P_1''}{P_F}\frac{(1-y_1'')}{(1-z_1)}}{1 - \frac{P_1''}{P_F}\frac{y_1''}{z_1}}\right] \quad (2)$$

which in the limit of (P_1'/P_F) and (P_1''/P_F) tending to zero becomes the ideal binary separation factor in an asymmetric permeator

$$\alpha_{12}^{*} = (\alpha_{12}^{'*}/\alpha_{12}^{"*}) \quad (3)$$

where $$\alpha_{12}^{'*} = (Pr_1'/Pr_2'),\ \alpha_{12}^{"*} = (Pr_1''/Pr_2'') \quad (4)$$

are the ideal separation factors for each membrane. Since $\alpha_{12}^{"*} < 1$ if species 1 preferentially goes through M' and species 2 perferentially goes through M", we have $\alpha_{12}^{*} > \alpha_{12}^{'*}$ (Ohno et. al. (3)), assuming $\alpha_{12}^{'*} > 1$.

If the asymmetric separator is such that $\dot{L} \neq o$ in Figure 1 for a binary mixture and the high pressure side gas composition in the perfectly mixed stage is x_i, we can still show that the value of α_{12}^{*} between streams $\dot{V}'$ and $\dot{V}''$ is given by relation (3). All one has to do is replace z_i by x_i in equations (1), (1a), (1b) and (2). In such a case, however, there arises a problem as to what is to be done with the reject stream of flow rate L especially if a cascade is being used.

Consider, however, a different situation where we have three components 1, 2 and 3 in the feed gas and $\dot{L} \neq o$. Suppose species 1 preferentially goes through M' and species 2 through

M" and the reject consists primarily of species 3. Suppose further that the stage is completely mixed such that the high pressure side composition is given by x_i'. Then, for membrane M', assuming binary permeabilities Pr_i' are valid here for species i, we have

$$y_1' \dot{V}' = [Pr_1' A_M'] [P_F x_1 - P_1' y_1'] \quad (5)$$

$$y_2' \dot{V}' = [Pr_2' A_M'] [P_F x_2 - P_1' y_2'] \quad (6)$$

$$y_3 \dot{V}' = [Pr_3' A_M'] [P_F x_3 - P_1' y_3'] \quad (7)$$

Further $x_1 + x_2 + x_3 = 1 = y_1' + y_2' + y_3'$. Defining α_1' as

$$\alpha_1' = \frac{y_1'}{(1 - y_1')} \frac{(1 - x_1)}{x_1} \quad (8)$$

we get

$$\alpha_1' = \frac{(1 - x_1)}{x_1} \left[\frac{Pr_1' P_F x_1 - P_1' y_1'}{P_F \{Pr_2' x_2 + Pr_3' x_3\} - P_1' \{Pr_2' y_2' + Pr_3' y_3'\}} \right] \quad (9)$$

Simplifying we get

$$\alpha_1' = \left[\frac{Pr_1'}{Pr_2'} \right] \frac{\left[1 - \frac{P_1'}{P_F} \frac{y_1'}{x_1} \right]}{\left\{ \frac{x_2}{(1-x_1)} + \frac{Pr_3'}{Pr_2'} + \frac{x_3}{(1-x_1)} \right\} - \frac{P_1'}{P_F} \left\{ \frac{y_2'}{(1-x_1)} + \frac{Pr_3'}{Pr_2'} \frac{y_3}{(1-x_1)} \right\}} \quad (10)$$

an expression which is preferred if $Pr_2' > Pr_3'$. On the other hand, if $Pr_3' > Pr_2'$, we would prefer

$$\alpha_1' = \frac{Pr_1'}{Pr_3'}\left[\frac{1 - \frac{P_1'}{P_F}\frac{y_1'}{x_1}}{\left\{\frac{x_2}{(1-x_1)}\frac{Pr_2'}{Pr_3'} + \frac{x_3}{(1-x_1)}\right\} - \frac{P_1'}{P_F}\left\{\frac{y_2'}{(1-x_1)}\frac{Pr_2'}{Pr_3'} + \frac{y_3'}{(1-x_1)}\right\}}\right] \quad (11)$$

Similarly, for membrane M", we can get using binary permeabilities Pr_i'' for species i,

$$\alpha_1'' = \frac{y_1''(1 - x_1)}{x_1(1 - y_1'')} \quad (12)$$

$$\alpha_1'' = \frac{Pr_1''}{Pr_2''}\frac{\left\{1 - \frac{P_1''}{P_F}\frac{y_1''}{x_1}\right\}}{\left\{\frac{x_2}{(1-x_1)} + \frac{Pr_3''}{Pr_2''}\frac{x_3}{(1-x_1)}\right\} - \frac{P_1''}{P_F}\left\{\frac{y_2''}{(1-x_1)} + \frac{Pr_3''}{Pr_2''}\frac{y_3''}{(1-x_1)}\right\}} \quad (13)$$

This form is preferred since $Pr_2'' > Pr_3''$ (already assumed for the problem). One can define several separations factors for species 1 with respect to others for the asymmetric permeator of Figure 1 with $\dot{L} \neq o$. One such separation factor is α_1' indicating the separation of species 1 from others between the permeate through M' and the reject stream $\dot{L}$ (consisting primarily of species 3). Another one is α_1''. A third separation factor would be

$$\alpha_1 = \frac{y_1'(1 - y_1'')}{(1 - y_1')y_1''} = \frac{\alpha_1'}{\alpha_1''} \quad (14)$$

The general expression for α_1 from relations (10) and (13), for example, is

$$\alpha_1 = \frac{Pr_1}{Pr_2'Pr_1''}\frac{Pr_2''}{}\left[\frac{1 - \frac{P_1'}{P_F}\frac{y_1'}{x_1}}{1 - \frac{P_1''}{P_F}\frac{y_1''}{x_1}}\right]\left[\frac{\left\{\frac{x_2}{(1-x_1)} + \frac{Pr_3''}{Pr_2''}\frac{x_3}{(1-x_1)}\right\} - \frac{P_1''}{P_F}\left\{\frac{y_2''}{(1-x_1)}\frac{Pr_3''}{Pr_2''}\frac{y_3''}{(1-x_1)}\right\}}{\left\{\frac{x_2}{(1-x_1)} + \frac{Pr_3'}{Pr_2'}\frac{x_3}{(1-x_1)}\right\} - \frac{P_1'}{P_F}\left\{\frac{y_2'}{(1-x_1)}\frac{Pr_3'}{Pr_2'}\frac{y_3'}{(1-x_1)}\right\}}\right] \quad (15)$$

When $P_1' << P_F$ and $P_1'' < P_F$, the ideal separation factor α_1^* is obtained. For the special case of $P_1' << P_F$, $P_1'' << P_F$, $Pr_3' << Pr_2' < Pr_1'$ and $Pr_2'' > Pr_1'' >> Pr_3''$, we obtain for α_1^*,

$$\alpha_1'^* = \frac{Pr_1'}{Pr_2'} \frac{(1-x_1)}{x_2} \tag{16}$$

$$\alpha_1''^* = \frac{Pr_1''}{Pr_2''} \frac{(1-x_1)}{x_2} \tag{17}$$

$$\alpha_1^* = \frac{Pr_1'}{Pr_2'} \frac{Pr_2''}{Pr_1''} = \frac{\alpha_{12}'^*}{\alpha_{12}''^*} \tag{18}$$

where the ideal binary separation factors for species 1 and 2 through membranes M' and M'' are given respectively by

$$\alpha_{12}'^* = (Pr_1'/Pr_2'), \quad \alpha_{12}''^* = (Pr_1''/Pr_2'') \tag{19}$$

Although $\alpha_{12}''^*$ is less than 1, $\alpha_1''^*$ need not be less than 1. If, however, $\alpha_1''^* < 1$ then $\alpha_1^* > \alpha_{12}'^*$ and the result is similar to the binary case. One should notice, however, that in the limit of $P_1' << P_F$ and $Pr_2' >> Pr_3'$, $\alpha_1'^*$ has, due to multicomponent nature of the problem, a form given by (16) which is different from $\alpha_{12}'^*$. Similarly for $\alpha_1''^*$ and $\alpha_{12}''^*$.

On the other hand, suppose $x_2 << x_3$ (due to, say, $z_2 << z_3$), $P_1' << P_F$, $P_1'' << P_F$, $Pr_3' \cong Pr_2'$ and $Pr_2'' >> Pr_3''$. In such a case, the form of α_1^* is obtained as follows:

$$\alpha_1 = \frac{y_1'}{(1-y_1')} \frac{(1-y_1'')}{y_1''} = \frac{y_1'}{(1-y_1')} \frac{(1-x_1)}{x_1} \frac{x_1}{(1-x_1)} \frac{(1-y_1'')}{y_1''} \tag{20}$$

$$\alpha_1^* \cong \frac{Pr_1'}{Pr_3'} \frac{(1-x_1)}{x_3} \frac{Pr_2''}{Pr_1''} \frac{x_2}{(1-x_1)}$$

$$\alpha_1^* \cong \left[\frac{Pr_1'}{Pr_3'}\right] \frac{1}{(\alpha_{12}''^*)} \frac{x_2}{x_3} \tag{21}$$

Obviously the value of α_1^* under these conditions is much less than that of α_1^* given by relation (18) since here $Pr_3' \cong Pr_2'$. Further, if $\alpha_{12}''^* \cong (x_2/x_3)$ due to $Pr_2'' >> Pr_1''$, then α_1^* is merely (Pr_1'/Pr_3') and no particular advantage is obtained from the asymmetric gas separator arrangement. Notice that the result (21) is also valid if in addition to the conditions mentioned for obtaining (21), $x_1 << x_3$. Under such conditions, the only advantage of an asymmetric permeator is its multicomponent separation ability. It must be mentioned however, that, if $Pr_1' >> Pr_3' \cong Pr_2'$ is valid in addition, then $\alpha_{12}'^*$ is quite large and consequently even if $x_2 << x_3$ and $\alpha_{12}''^*$ (x_2/x_3), α_1^* is large.

STAGE ANALYSIS: CROSSFLOW ASYMMETRIC PERMEATOR

Consider Figure 4 where a crossflow asymmetric permeator has been shown. For a length dl in the mean flow direction at any location of an asymmetric permeator, the mass balance for species 1 and 2 for a 3-component system will lead to, for negligible axial diffusion and no axial mixing,

$$d\dot{V}' y_1' + d\dot{V}'' y_1'' = \dot{L}\, dx_1 + x_1\, d\dot{L} \qquad (22)$$

$$d\dot{V}' y_2' + d\dot{V}'' y_2'' = \dot{L}\, dx_2 + x_2\, d\dot{L} \qquad (23)$$

where $\dot{L}$ is the high pressure side feed flow rate at that location and x_1, x_2 and x_3 are the local mole fractions of species 1, 2 and 3 respectively in the high pressure L stream. Rearranging these two relations, we obtain

$$d\dot{V}' (y_1' - x_1) + d\dot{V}'' (y_1'' - x_1) = \dot{L}\, dx_1 \qquad (24)$$

$$d\dot{V}' (y_2' - x_2) + d\dot{V}'' (y_2'' - x_2) = \dot{L}\, dx_2 \qquad (25)$$

since

$$d\dot{L} = d\dot{V}' + d\dot{V}'' \qquad (26)$$

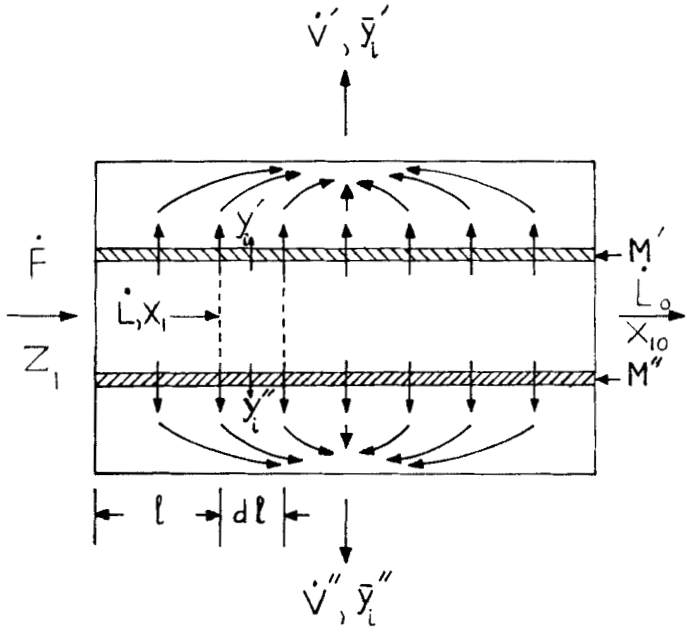

FIGURE 4. ASYMMETRIC PERMEATOR-CROSSFLOW STAGE ANALYSIS

Analytical integration of these equations along the permeator is, perhaps, impossible unless simplifications are made. One such case would be: M' is essentially impermeable to species 2; feed is dilute in 1 and 2, M'' is essentially impermeable to species 1; species 3 is impermeable through M' and M''; $d\dot{V}'$ is of the same order of magnitude as $d\dot{V}''$. Therefore

$$y_1'' \cong o \; ; \; y_2' \cong o \; ; \; x_1, x_2 \ll 1; \; y_3' \cong y_3'' \cong o; \; d\dot{V}' = O(d\dot{V}'') \quad (27)$$

Then we have equations (22) and (23) simplified to

$$d\dot{V}' \, y_1' = \dot{L} \, dx_1 + x_1 \, d\dot{L} \quad (28)$$

and

$$d\dot{V}'' \, y_2'' = \dot{L} \, dx_2 + x_2 \, d\dot{L} \quad (29)$$

Therefore

$$\begin{aligned} d\dot{V}' \, y_1' &= \dot{L} \, dx_1 + x_1 \, (d\dot{V}' + d\dot{V}'') \\ &\cong \dot{L} \, dx_1 + x_1 \, d\dot{V}' \end{aligned} \quad (30)$$

and $$\frac{\dot{dV}'}{\dot{L}} = \frac{dx_1}{(y_1' - x_1)} \tag{31}$$

Similarly $$\frac{\dot{dV}''}{\dot{L}} = \frac{dx_2}{(y_2'' - x_2)} \tag{32}$$

Adding the two equations (31) and (32) we have

$$\frac{\dot{dL}}{\dot{L}} = \frac{\dot{dV}'}{\dot{L}} + \frac{\dot{dV}''}{\dot{L}} = \frac{dx_1}{(y_1' - x_1)} + \frac{dx_2}{(y_2'' - x_2)} \tag{33}$$

Analytical integration of this equation is possible along the length of the permeator if one assumes that the separation factors for species 1 through M' and species 2 through M'' respectively are constant along the permeator. Here we define

$$\alpha_1' = \frac{y_1'(1 - x_1)}{(1 - y_1')x_1} \quad \text{and} \quad \alpha_2'' = \frac{y_2''(1 - x_2)}{x_2(1 - y_2'')} \tag{34}$$

as in the definitions (8) and (12). Adopting then Naylor and Backer's (5) approach valid for constant separation factors α_1' and α_2'', define

$$\varepsilon_1' = (\alpha_1' - 1), \quad \varepsilon_2'' = (\alpha_2'' - 1) \tag{35}$$

Since $$y_1' - x_1 = \left[\frac{x_1 \varepsilon_1'(1-x_1)}{1 + \varepsilon x_1}\right] \tag{36}$$

and similarly for $y_2'' - x_2$, we integrate equation (33) from the location under consideration to the end of the permeator where the reject flow rate and compositions are given by L_o, x_{io} This yields

$$\int_{\dot{L}}^{\dot{L}_o} \frac{d\dot{L}}{\dot{L}} = \ln\left[\frac{\dot{L}_o}{\dot{L}}\right] = \int_{x_1}^{x_{10}} \frac{(1+\varepsilon_1' x_1)dx_1}{x_1\varepsilon_1'(1-x_1)} + \int_{x_2}^{x_{20}} \frac{(1+\varepsilon_2'' x_2)\,dx_2}{x_2\varepsilon_2''(1-x_2)} \quad (37)$$

$$\dot{L} = \dot{L}_o\left[\left\{\frac{x_1}{x_{10}}\right\}^{\frac{1}{\varepsilon_1'}}\left\{\frac{x_2}{x_{20}}\right\}^{\frac{1}{\varepsilon_2''}}\left\{\frac{1-x_{10}}{1-x_1}\right\}^{\frac{\alpha_1'}{\alpha_1'-1}}\left\{\frac{1-x_{20}}{1-x_2}\right\}^{\frac{\alpha_2''}{\alpha_2''-1}}\right] \quad (38)$$

after considerable rearrangement. Assuming that the location under consideration is the stage inlet, then there are three unknowns in equation (38) if inlet conditions are known: $\dot{L}_o$, x_{10} and x_{20}. Since by assumption (27) $y_1'' \cong o$ and $y_2' \cong o$, if we, in addition assume that $P_F \gg P_1'$, $P_F \gg P_1''$, then in the length dl,

$$\begin{aligned} y_1'\,d\dot{V}' &= Pr_1'(dA_M')\left[P_F x_1 - P_1' y_1'\right] \cong Pr_1' P_F x_1 (dA_M') \\ y_2''\,d\dot{V}'' &= Pr_2''(dA_M'')\left[P_F x_2 - P_1'' y_2''\right] \cong Pr_1'' P_F x_2 (dA_M'') \end{aligned} \quad (39)$$

and

$$\frac{y_1'}{y_2''}\frac{d\dot{V}'}{d\dot{V}''} = \frac{Pr_1'}{Pr_2''}\frac{x_1}{x_2} = \frac{dx_1}{(y_1'-x_1)}\frac{(y_2''-x_2)}{dx_2}\frac{y_1'}{y_2''} \quad (40)$$

where we have assumed $dA_M' = dA_M''$ for the length dl of the permeator and used the relations (31) and (32). Thus

$$\int_{x_1}^{x_{10}} \frac{y_1'\,dx_1}{x_1(y_1'-x_1)} = \int_{x_2}^{x_{20}} \frac{y_2''\,dx_2}{x_2(y_2''-x_2)} \left\{\frac{Pr_1'}{Pr_2''}\right\} \quad (41)$$

These can be analytically integrated easily and a relation ob-

tained between x_{10} and x_{20} for given inlet concentrations. Thus, for any given x_{10}, x_{20} is known and this will yield the value of $\dot{L}_o$ from equation (38). The membrane area of M' membrane, for example, may now be obtained for known $\dot{L}_o$, x_{10} and x_{20}. The first step is to obtain a relation between x_1 and x_2 from (41) for known x_{10} and x_{20}. Then substitute for x_2 this expression in terms of x_1 in relation (38). Next combine equations (31) and (39) to obtain

$$A_M' = \int dA_M' = \frac{1}{Pr_1' P_F} \int_{x_1=z_1}^{x_{10}} \frac{(y_1' \dot{L}) \, dx_1}{(y_1' - x_1) x_1} \qquad (42)$$

Here y_1' can be related to x_1 through definition (34) and the expression for $\dot{L}$ is obtained from the result (38) in terms of x_1. Thus the area of membrane M' can be determined; similarly for membrane M''. Perhaps, numerical integration would be necessary since due to the complex nature of the integrand, we have not attempted an analytical solution here. Neither have we attempted here to apply other well-known methods used for cross-flow no mixing stages for a binary system. For symmetric permeators, these are well treated in Stern and Walawender (6) for binary gas mixtures. Obviously, other flow patterns in asymmetric permeators will lead to a quite complicated situation.

We have not considered here continuous membrane columns of Hwang and Thorman (4) with different membranes at different and/or same locations. Obviously multicomponent separators with such arrangements having countercurrent flow and recycle are possible.

POSSIBLE GAS SEPARATION APPLICATIONS OF ASYMMETRIC PERMEATORS

Besides the rare gas separation applications by Ohno et. al. (3), no known example of asymmetric separator is available for gas separations. However, the following processes certainly appear to be worthy of exploration. Consider the multicom-

ponent gas mixture, the synthesis gas, needed for ammonia production. It contains CO as well as CO_2 in addition to N_2, H_2 etc. Usually CO is converted to CO_2 by shift reaction to produce the necessary amount of H_2. With an asymmetric permeator having two different immobilized liquid membranes, it is likely that CO and CO_2 can be eliminated separately from this gas mixture without difficulty. Further, the separated CO can be reacted with low temperature steam to produce hydrogen and CO_2 with the latter removed by one of several means available. There are various highly efficient immobilized facilitated liquid membranes for CO_2 removal (Ward (7)). For CO removal, the same reference indicates the possibility of using cuprous ions in a suitable solution (containing, say, cuprous ammonium formate) which will facilitate the CO transport through an immobilized liquid film in the manner of facilitated transport of NO by a solution containing ferrous ions (8). Since the separation factor for each species CO_2 and CO through membranes M' and M'' is large, the previous analysis is likely to be valid for the case. Further, since the post-shift reactor gas is cooled anyway for CO_2 absorption, the cooling may be carried out earlier to eliminate the problem of liquid membrane evaporation. Such an asymmetric permeator opens up interesting possibilities for improvements in process design for synthesis gas.

It is possible to conceive of binary separations other than rare gas separations through an asymmetric permeator also. Some typical systems for these are CO_2-CH_4 mixture form sewage treatment or biomass processes, H_2S-CO_2 mixtures from coke ovens, refineries etc. However, the separation factor of CO_2 over CH_4 and H_2S over CO_2 through many of the facilitated liquid membranes are large enough (7) to reduce the need for an asymmetric permeator.

ASYMMETRIC PERMEATOR FOR LIQUID SEPARATIONS

A hypothetical example of an asymmetric permeator demonstrating some of its advantages will now be treated in the

context of any desalination problem. Whereas reverse osmosis is routinely employed now-a-days for desalination with polyamides, PA-300, and cellulose acetate membranes, piezodialysis is not yet a practical desalting process. However, piezodialysis membranes developed thus far (9) (10), are capable of substantial salt enrichment in the permeate and workers in this area have suggested piezodialysis to be "on the verge of being a practical desalting process" (9). Assuming then that improved piezodialysis (PD) membranes will be available in flat sheet or hollow fiber form, asymmetric permeators are possible with flat reverse osmosis (RO) desalination and piezodialysis membranes as in Figure 1 or with hollow fiber membranes as in Figure 2. For a binary separation like desalination, we would now like to show that such asymmetric desalinators have two distinct features:

1. The rise in bulk salt concentration of the high pressure feed along the length of such a permeator is much less than that in a permeator using only RO membranes and having the combined area of RO and PD membranes used in an asymmetric permeator. In fact, depending on how improved the PD membrane is and the relative area ratio of the PD membrane with respect to RO membrane, the bulk salt concentration may even decrease along the length of the permeator. This, of course, implies that lower pressures of operation are possible for a given feed and a desired amount of water recovery since the osmotic pressure of the concentrated brine to be rejected often determines the pressure of operation.

2. The concentration polarization problem is likely to be reduced since the salt concentration at the PD membrane surface is much less than the bulk salt concentration. While this is of no importance in membrane channels which are reasonable thick, it is of great importance in hollow fiber modules. Since the inter-fiber distance in a hollow fiber module is extremely small, the gradient in salt concentration from the wall of a RO

hollow fiber to the wall of an adjacent PD hollow fiber will be much higher resulting in a much lower level of concentration polarizaiton. Although Hermans (11) has pointed out that the severity of concentration polarizaiton in hollow fiber RO units is likely to be limited due to the low flux level etc., as long as PD hollow fibers are present in 1:1 ratio with RO hollow fibers in an asymmetric permeator, the concentration polarization is likely to be much less than that in a hollow fiber RO unit.

The asymmetric permeator concept, as originally introduced (3), resulted in an increased stage separation factor for low separation factor cases. Therefore, although, there is no apparent reason for having an asymmetric permeator for a high separation factor process like reverse osmosis desalination, the above discussion suggests ample basis for further study. We now carry out some preliminary calculations to illustrate our point.

Consider in Figure 4 a small length dl of the asymmetric permeator for desalination at any location where the volumetric feed brine flow rate is $\dot{F}_v$ and feed brine salt concentration is C_{sf}. If the RO side molar output through membrane M' of length dl and area dA_M' per unit time is

$$d\dot{V}' = (N_w^{RO}\, dA_M' + N_s^{RO}\, dA_M') \tag{43}$$

and the PD side output through membrane M'' of length dl and area dA_M'' per unit time is

$$d\dot{V}'' = (N_w^{PD} + N_s^{PD})\, dA_M'' \tag{44}$$

then the ratio of volume of purified water recovered over the increase in salt concentration in length dl of the asymmetric permeator is given as

$$(\text{Ratio})_{\text{Asym}} = \frac{\left[N_w^{RO}(dA_M' + p\,dA_M'')\bar{V}_w\right]\left[\dot{F}_v - N_w^{RO}(dA_M' + p\,dA_M'')\bar{V}_w\right]}{\left[C_{sf}\,\bar{V}_w\,N_w^{RO}(dA_M' + p\,dA_M'') - N_s^{RO}dA_M' - N_s^{PD}dA_M''\right]} \tag{45}$$

where

$$N_w^{PD} = p\,N_w^{RO},\quad p \ll 1 \tag{46}$$

For a symmetric permeator with only RO membranes and having the same feed at the same location, the same ratio will be changed to

$$(\text{Ratio})_{\text{Sym}} = \frac{\left[N_w^{RO}(dA_M' + dA_M'')\bar{V}_w\right]\left[\dot{F}_v - N_w^{RO}\,\bar{V}_w(dA_M' + dA_M'')\right]}{\left[C_{sf}\,\bar{V}_w\,N_w^{RO}\,(dA_M' + dA_M'') - N_s^{RO}\,(dA_M' + dA_M'')\right]} \tag{47}$$

since for this case $p = 1$ and $N_s^{PD} = N_s^{RO}$. If we take the following ratio $(\text{Ratio})_{\text{Asym}}/(\text{Ratio})_{\text{Sym}}$ and assume that the RO membrane is quite tight so that $C_{sp} = o$, we will get for the case $dA_M' = dA_M''$

$$\frac{(\text{Ratio})_{\text{Asym}}}{(\text{Ratio})_{\text{Sym}}} = \left[\frac{1 - \dfrac{(1+p)\,N_w^{RO}\,\bar{V}_w\,dA_M'}{\dot{F}_v}}{1 - \dfrac{2\,N_w^{RO}\,\bar{V}_w\,dA_M'}{\dot{F}_v}}\right]\left[1 - \frac{1}{\dfrac{N_s^{PD}}{N_w^{RO}\,(1+p)C_{sf}\,\bar{V}_w}}\right] \tag{48}$$

Usually $p \ll 1$, so that although dA_M' is a differential quantity, the first term within brackets on the right hand side is greater than 1. Further, the second term is always greater than 1 and as the piezodialysis membrane performance improves, its value will become greater. Thus, in an asymmetric permeator, the increase in salt concentration along the permeator is going to be less than that in a symmetric reverse osmosis desalinator for a given water production rate.

One could go a step further. For a batch well stirred asymmetric desalinator with a RO membrane area A_M', a PD membrane area A_M'', feed salt mole fraction x_{sf} and product salt mole fractions y_s' and y_s'' (at any time), the condition for no increase in x_{sf} as desalination proceeds may be easily shown to be

$$\frac{A_M''\left[N_s^{PD} + N_w^{PD}\right]}{A_M' \quad N_w^{RO}} = \frac{x_{sf} - y_s'}{y_s'' - x_{sf}} \cong \frac{1}{\dfrac{y_s''}{x_{sf}} - 1} \qquad (49)$$

where we have assumed $y_s' << x_{sf}$ and $x_{wf} \cong y_w'' \cong y_w'$. Thus, the higher is the permeability of salt through the PD membrane, and the higher is the salt enrichment through the PD membrane, the lower will be the ratio (A_M''/A_M') required to maintain constant feed salt concentration. Otherwise, A_M'' will have to be many times larger than A_M'. Thus, order of magnitude improvements are necessary in flux values through PD membranes before they are useful in asymmetric permeators for achieving constant salt concentrations since the current values are low (the PD membranes being far from the asymmetric type) (9).

It is possible to conceive of other binary systems for which asymmetric permeators may be useful. For example, for the phenol-water system, it is known (12) that cellulose acetate membranes may have a negative rejection of phenol up to 20% whereas polyamide membranes used in a B-9 permeator have 55% rejection of phenol (13) at a pH of 7-9. Thus purified water and phenol-rich water are obtained simultaneously with the phenol-rich water having a higher concentration of phenol than what would have been obtained by a symmetric permeator with polyamide membranes only. Similarly for a feed mixture of polar and non-polar substances like alcohols and hydrocarbons, an asymmetric permeator with a polyethylene (PE) and a polar membrane (poly-

amides or cellulose acetate) will produce a highly hydrocarbon rich fraction through the PE membrane whereas an alcohol rich fraction will be obtained through the other membrane (provided it does not swell and get destroyed by the hydrocarbon) (14).

CONCLUSIONS

The concept of an asymmetric permeator utilizing two different membranes which enrich two different nonionic species from a gaseous mixture or a liquid solution has a number of interesting implications. For a binary feed, such a permeator has a higher separation factor than one with a single type of membrane. For a ternary or multicomponent feed in general with the two membranes being specific to two species, such a permeator has multicomponent separation capabilities and yields three fractions enriched in three species. For a high separation factor process like reverse osmosis desalination, an asymmetric permeator with a reverse osmosis membrane and piezodialysis membrane has a reduced increase in salt concentration along the permeator length thus raising the likelihood of desalination at a lower pressure. Proximity of piezodialysis hollow fiber membrane to a reverse osmosis hollow fiber membrane is likely to reduce concentration polarization significantly. Although the possibilities of a number of interesting new or improved separations has been indicated, the stage analysis of an asymmetric permeator is much more complicated than that of a symmetric permeator.

SYMBOLS

A_M	membrane area in the permeator
C_{sf}	molar concentration of salt in feed brine
C_{sp}	molar concentration of salt in permeate from RO membrane
dA_M	differential membrane area for permeator length dl
dl	differential length of the permeator
dL	differential change in L for length dl

$\dot{dV}$ molar rate of permeate production for length dl

$\dot{F}$ molar feed flow rate at permeator inlet

$\dot{F}_v$ volumetric brine feed flow rate at permeator inlet

L molar feed flow rate at location l in the permeator

M', M'' two different membranes in the asymmetric permeator

N_i^{PD} molar flux of species i through a piezodialysis membrane, i = w for water and i = s for salt

N_i^{RO} molar flux of species i through a reverse osmosis membrane, i = w for water and i = s for salt

P_F high pressure on the feed side of permeator

P_l low pressure on the permeate side of permeator

Pr_i permeability of gas species i through membrane, i = 1,2,3

$\dot{V}$ molar rate of permeate production

$\bar{V}_w$ partial molar volume of water

x_i mole fraction of species i at the outlet of a perfectly mixed gas permeator or at any location of the feed side of a crossflow gas permeator, i = 1,2,3

x_{if} mole fraction of species i in high pressure brine feed, i = w for water and i = s for salt

y_i mole fraction of species i in permeate, i = 1,2,3 for gas permeator, i = s,w for salt and water in desalination

z_i mole fraction of species i in feed to a gas permeator

Greek letters

α_l separation factor for species l in asymmetric separator, definition (14)

α_l^* ideal separation factor for species l in an asymmetric separator, definitions (21), (18)

α_l' separation factor for species l through membrane M', definition (8), (34)

α_l'' separation factor for species l through M'', definition (12)

α_2'' separation factor for species 2 through M'', definition (34)

$\alpha_1'^*, \alpha_1''^*$ defined respectively by (16) and (17)

α_{12} defined by (1), binary stage separation factor for species 1,2

$\alpha_{12}'^*, \alpha_{12}''^*$ defined by (4) and (19), ideal binary separation factors through membranes M' and M"

α_{12}^* ideal binary stage separation factor for species 1,2, definition (3)

$\varepsilon_1', \varepsilon_2''$ defined by (35)

Subscripts

i species 1, 2 and 3

o stage exit conditions

Superscripts

' relates to membrane M'

" relates to membrane M"

* ideal conditions with permeate side pressures being too low compared to feed pressure.

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