Effect of Viscosity on Concentration Polarization in Ultrafiltration

William N. Gill
Department of Chemical Engineering
Rennselaer Polytechnic Institute
Troy, NY 12180

Diane E. Wiley,
Christopher J.D. Fell,
Anthony G. Fane
School of Chemical Engineering
and Industrial Chemistry
University of New South Wales
Kensington, N.S.W. 2033 Australia

Ultrafiltration systems, which separate macromolecular solutions by using pressure to drive the solvent through a membrane, usually operate in the range of 10^5 to 10^6 Pa and for small applied pressures the solvent flux is proportional to the pressure. As the operating pressure is increased the flux reaches an asymptotic value beyond which a further increase in the pressure does not produce an increase in the flux. This behavior usually is attributed to:

1) Build-up solute molecules at the solution-membrane interface, known as concentration polarization

2) Gel formation which occurs when the concentration at the membrane surface reaches a sufficiently high level

Clearly, the optimum operation of ultrafiltration systems is highly dependent on the management of concentration polarization. Thus, it is desirable to understand the mechanisms which control it by examining the transport equations given by Bird et al. (1960).

Sherwood et al. (1965) and Dresner (1964) first recognized the importance of concentration polarization in reverse osmosis systems. Gill et al. (1966), (1972) and Brian (1965) showed that osmotic pressure effect due to increased concentration causes the flux to decrease with downstream distance. Derzansky and Gill (1974) demonstrated by experiments that natural convection can become the controlling mechanism which sets the level of concentration polarization downstream in crossflow reverse osmosis. Doshi et al. (1971) considered the effects of variable viscosity and diffusivity in reverse osmosis separations of NaCl and sugar in water in which the fluxes are relatively low and the physical property variations are rather weak. The much lower fluxes, high diffusivities and lower concentration polarization levels make gel formation of less concern in reverse osmosis than in ultrafiltration.

Blatt et al. (1970) successfully compared the several qualitative features of the gel polarization model with ultrafiltration data. However, Fane et al. (1981) indicated that membrane properties can affect the limiting flux mentioned previously and they proposed a model to account for membrane heterogeneity.

The ultrafiltration of solutions with variable fluid properties has been considered by Kozinski and Lightfoot (1971) for stagnation flow. Shen and Probstein (1977) used a similarity approach with constant interfacial concentrations to determine the limiting flux in crossflow ultrafiltration. For them, using a constant viscosity affected their value of V_w only up to 50% because the interfacial concentration was constant at the limiting flux condition they studied. They assumed that the concentration at the interface was constant from the inlet of the system and equal to the value required for gelling to occur. Our approach is different from and complementary to theirs. In effect, Shen and Probstein neglect the entrance length over which the interfacial concentration changes from the inlet value, C_o, to the value C_g, at which a gel forms. We determine this entrance length. The question we ask is how does the viscosity variation with concentration affect the level of polarization for a given fraction of feed removed in crossflow ultrafiltration? That is, our analytical model accounts for the increase in viscosity due to concentration polarization, which causes the flow near the membrane to slow down and further exacerbates the increase of polarization. The model shows, to a first approximation at least, that a feedback loop can be established in which variable viscosity greatly increases polarization to the extent that a "blow-up" occurs and thereby plays an important role in rendering unproductive substantial downstream portions of crossflow ultrafiltration systems.

The affects of variable diffusivity is to exacerbate this polarization problem for a given flux, and to cause C_g to be reached at even shorter distances assuming that the diffusion coefficient decreases with increasing concentration. Once C_g is achieved at some distance, x, one would expect the interfacial concentration to remain constant, and beyond that value of x the analysis of Shen and Probstein provides a means of estimating how the flux decreases. A complete treatment of the overall problem requires a numerical analysis because C_g is achieved at a finite distance from the entrance and therefore at a finite value of the diffusion boundary layer thickness.

Analysis

The convective diffusion equation is

$$u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} = \frac{\partial}{\partial y}D\frac{\partial c}{\partial y} \tag{1}$$

and since the Schmidt number is very high and the diffusion boundary layer is very thin the boundary conditions are

$$c(o, y) = c(x, \infty) = c_o \tag{2a}$$

$$D_w\frac{\partial c}{\partial y}(x, o) + v_w c(x, o) = 0 \tag{2b}$$

There has been a number of published solutions to this set of equations for constant fluid properties. Dresner (1964) used a linearized velocity and the Laplace transform to obtain an approximate analytical solution, which near the channel entrance is given by

$$\frac{c_w}{c_o} = 1 + 1.536\left(\frac{\xi}{9}\right)^{1/3} \tag{3a}$$

and further downstream by

$$\frac{c_w}{c_o} = 1 + \frac{\xi}{9} + 5(1 - e^{-\sqrt{\xi/27}}) \tag{3b}$$

Brian (1965) and Sherwood et al. (1963, 1965) and Gill et al. (1966) showed that the simple approximate result given in Eq. 3 is both accurate and useful. Brian's (1965) work also showed that by interpreting results in terms of fractions of feed removed, constant flux results can be used as a first approximation for variable flux conditions.

Table 1 lists the variation of density, viscosity and diffusivity over a wide range of concentrations for solutions typically used as model compounds in ultrafiltration studies. In practice, one may begin with a very dilute solution (0.1% or 1% wt.) which produces a gel-polarized condition at the wall (40% wt. or more) for some point not too far downstream. Therefore, solution properties are considered over this whole range to gain an accurate picture of real systems.

From the table it is obvious that the variations in density are negligible. As suggested by the Wilke-Chang theory, the variations in viscosity and diffusivity are inversely proportional at low concentrations for some substances, but not for all substances. Significant deviations from this theory occur when the concentration of the solute increases. For the systems reviewed it is clear that variations in viscosity are much larger than those in diffusivity. For example, with BSA, the data in Table 1 show that the viscosity increases by a factor of 50 while the diffusivity decreases by less than a factor of 2 when the concentration increases from 0.1 to 40% wt. Nevertheless, we shall estimate the effect of D as well.

Our solution is derived assuming that density is constant but diffusivity and viscosity vary with concentration. To obtain a simple and sharp first approximation which retains the essential nonlinear feedback nature of the process the flux is also assumed to be constant, i.e., $v = v_w$. The usual additional assumptions associated with the high Schmidt numbers of macromolecular

Table 1. Solution Properties for Common Macromolecules*

Solute	Concentration wt. %	Density 10^{-3} kg · m^{-3}	Viscosity 10^3 Pa · s	Diffusivity 10^{11} m^2 · s^{-1}
BSA	0.1		1.0	7.093
	1.0	1.003**	1.0	7.026
	5.0	1.015	1.1	6.740
	10.0	1.028	1.3	6.402
	15.0	1.040	1.7	6.082
	20.0		2.7	5.782
	40.0		49.6	4.745
Sucrose	0.5	1.000	1.0	
	1.0	1.002	1.0	
	10.0	1.038	1.2	
	20.0	1.081	1.7	
	40.0	1.177	4.5	
Dextran	0.5	1.000	1.0	4.108
	1.0	1.002	1.2	4.188
	5.0	1.017	2.8	5.810
	10.0	1.037	6.9	7.812
	15.0		14.7	8.063
	20.0		29.2	8.079

*From Clifton et al. (1984), Kozinsky and Lightfoot (1972), and Weast (1985).
**Values are for human serum; values for rabbit or guinea pig serum are similar.

solutions are made because the boundary layers are thin and the region of most interest therefore is close to the wall. Thus,

i) The cross-flow velocity can be expanded as a Taylor series and truncated after the second term to give:

$$u = u_w + \left(\frac{\partial u}{\partial y}\right)_w y \text{ (where } u_w = 0) \tag{4}$$

ii) If the flow is fully developed, Eq. 20 of Doshi et al. (1971) applies:

$$u^+ = \left(1 - \int_0^{x^+} v_w^+ \, dx^+\right) \frac{\displaystyle\int_0^{y^+} \frac{1 - y^+}{\mu^+} dy^+}{\displaystyle\int_0^1 \int_0^{y^+} \frac{1 - y^+}{\mu^+} dy^+ \, dy^+} \tag{5}$$

iii) The system may be regarded as semiinfinite.

iv) The value of D is taken to be that at the wall, D_w.

Combination of Eqs. 1, 4, and 5 gives:

$$\frac{3u_o}{h} y \frac{\partial c}{\partial x_1} - \frac{v_w}{D_w^+} \frac{\partial c}{\partial y} = D_o \frac{\partial^2 c}{\partial y^2} \tag{6}$$

where

$$x_1 = 3 \int_0^x D_w^+ u_w^+ \, dx \int_0^1 \int_0^{y^+} \frac{1 - y^+}{\mu^+} dy^+ \, dy^+ \tag{7}$$

The virtue of the transformation given by Eq. 7 is that it leads to Eq. 6 but it retains the full variability of crossflow, u, with respect to viscosity, μ. Equation 6 and boundary condition (Eq. 2b) have exactly the same form as the equation which Dresner (1964) solved for the case of *constant fluid properties* if we consider V_w/D_w constant. By analogy with Eq. 3 one gets:

$$\frac{c_w}{c_o} = 1 + 1.536 \left(\frac{\xi_1}{9}\right)^{1/3} \tag{8a}$$

and

$$\frac{c_w}{c_o} = 1 + \frac{\xi_1}{9} + 5(1 - e^{-\sqrt{\xi_1/27}}) \tag{8b}$$

where

$$\xi_1 = 3 \frac{x_1}{h} \left(\frac{v_w}{u_o}\right) \left(\frac{v_w h}{D_o}\right)^2 \tag{9}$$

Equation 7 may be used to relate x_1 (which contains the full dependence of viscosity on concentration) to x (the real length downstream). This equation can be simplified further by recognizing that, due to the thin diffusion boundary layers, the viscosity is equal to the bulk viscosity over much of the channel. Unless the viscosity in the boundary layer is extremely high, the major contribution to the integral in the denominator is therefore from $\mu = \mu_o$. Consequently,

$$\int_0^1 \int_0^{y^+} \frac{1 - y^+}{\mu^+} dy^+ \, dy^+ \approx \frac{1}{3} \tag{10}$$

so that

$$x_1 \approx \int_0^x D_w^+ \mu_w^+ \, dx \tag{11}$$

Combining Eqs. 9 and 11 gives

$$\xi_1 \approx 3 \left(\frac{v_w}{u_o}\right)^2 \frac{\displaystyle\int_0^x D_w^+ \mu_w^+ \, dx}{h} \tag{12}$$

Differentiation of Eq. 12 yields

$$\frac{d\xi_1}{dx} = 3 \left(\frac{v_w}{u_o}\right) \left(\frac{v_w h}{D_o}\right)^2 \frac{\mu_w^+ D_w^+}{h} \tag{13}$$

which, on integration, gives the equation

$$\frac{x}{h} = \frac{1}{3} \left(\frac{u_o}{v_w}\right) \left(\frac{D_o}{v_w h}\right)^2 \int_0^{\xi_1} \frac{d\xi_1}{D_w^+ \mu_w^+} \tag{14}$$

We see that the effect of the concentration dependence of D_w in the term V_w/D_w, assuming D_w decreases with concentration, is to decrease the effective flux for which one computes the relationship between C_w^+ and x/h, or to increase the polarization for a given flux. On the other hand, the effect of D_w in Eq. 14 is to increase the value of x/h for which we compute a particular C_w^+. These are opposite effects which tend to cancel one another. Furthermore, since the variation of D_w is much smaller than that of μ_w, in this preliminary calculation we will take $D_w^+ = 1$. It probably would be more accurate to use the value of D_w^+ corresponding to the average between C_o and C_g where C_g is the gelling concentration. However, since our purpose is to demonstrate that a "blowup" in concentration polarization may occur, the variation in D_w does not seem to affect the qualitative nature of this phenomenon.

If viscosity is known as a function of concentration [i.e., $\mu = \mu(c)$], Eqs. 8 and 14 can be used to calculate the wall concentration at any point downstream. Note that if we interpret v_w to be the average flux through the membrane, then $(v_w x/u_o h)$ is the fraction of feed removed for both constant or variable flux cases.

Choice of Viscosity Function

The equations used to relate viscosity (in Pa · s) to concentration (in % wt.) for the three macromolecules considered in subsequent sections of this paper are:

For sucrose

$$\mu = 0.0009049 \exp(0.03479\, c) \tag{15}$$

For BSA

$$\mu = 0.0009086 \exp(0.00244\, c^2) \tag{16}$$

For dextran

$$\mu = 0.0009086\, [1 + 0.01\, c \exp(0.08678\, c + 3.313)] \tag{17}$$

The equations used for BSA and dextran are those employed by Kozinski et al. (1972) and Clifton et al. (1984), respectively. That used for sucrose was obtained by performing a regression analysis on data available in the *CRC Handbook* (1985). All appear to be adequate for concentrations at least up to 40% wt.

Results

Figure 1 shows the variation of the dimensionless wall concentration $c_w^+ = c_w/c_o$ as a function of the dimensionless variable $\xi = 3\,(x/h)(v_w h/D_o)^2\,(v_w/u_o)$. Values of c_w^+ calculated assuming that viscosity is constant are compared with those calculated assuming that viscosity varies with concentration, for sucrose, BSA and dextran, at several values of the inlet concentration. First, it is obvious that, for each of the macromolecules, an increase in the flux (v_w) or channel height (h) or a decrease in the crossflow (u_o) will produce a higher concentration at the wall for a fixed distance downstream. Second, an increase in the inlet concentration increases the concentration nonlinearly if all other variables are held constant. Finally, there is a significant difference between the values for c_w^+ obtained assuming constant and variable viscosity particularly at the higher inlet concentrations. The effect is more pronounced for those species which show a greater dependence of viscosity on concentration. Thus $c^+_{w\,\mathrm{dextran}} > c_w^+$ BSA $c^+_{w\,\mathrm{sucrose}}$ for the same value of ξ and c_o because, at this value, $\mu^+_{w\,\mathrm{dextran}} > \mu_w^+$ BSA $> \mu^+_{w\,\mathrm{sucrose}}$.

Figure 1 is essentially a multiparameter representation of a large number of other graphs which could be drawn illustrating the effect of a single parameter on the wall concentration. For example, Figure 2 shows, for BSA, the effect of a variation in the flux on the distance downstream at which certain values of c_w^+ will be attained, when the crossflow, inlet concentration and channel height are constant. The significant difference between the constant and variable viscosity model is again obvious. It is true that, under reverse osmosis conditions ($v_w = 1 \times 10^{-6}$ m · s^{-1} = 3.6 1 m^{-2} · h^{-1}), there is a negligible difference between the two models and, as is expected, the wall concentration is only two to three times that of the bulk solution at the end of most conventional channels. However, as the flux is increased and the diffusion coefficient decreases to those more typical of ultrafiltration the difference between the two models becomes important. Thus, for a flux of 1×10^{-5} m · s^{-1} (36 1 m^{-2} · h^{-1}), the constant viscosity model predicts that gel-polarization (that is, a wall concentration of the order of 40% wt. for BSA) will be achieved at a distance of 50 cm from the entrance, but the variable viscosity model predicts that this will occur at a distance of only 19 cm from the entrance.

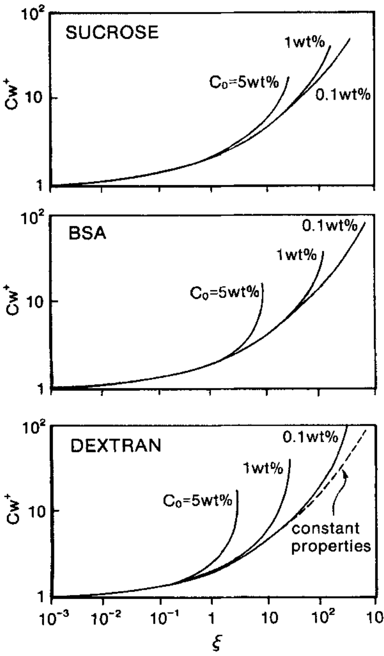

Figure 1. Dimensionless wall concentration as a function of ξ for sucrose, BSA and Dextran with initial concentrations, C_o, of 5, 1, 0.1 wt. %.

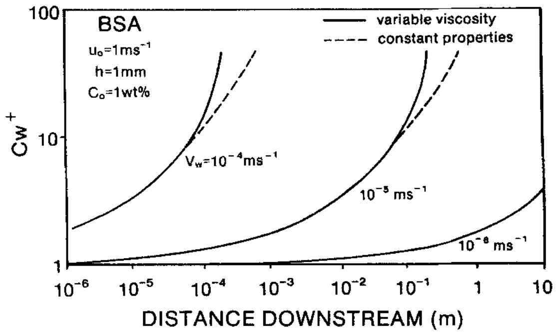

Figure 2. Downstream distance from entrance with initial concentration, C_o, of BSA equal 1 wt. % and wall fluxes, v_w, equal 10^{-4}, 10^{-5}, 10^{-6} m · s^{-1}, or 360, 36, 3.6 1 M^{-2} · h^{-1}.

For reverse osmosis systems, constant property calculations are satisfactory, and the solution of Dresner (1964) for constant flux is reasonably accurate and convenient to use. Once, however, the conditions start to approach those more typical of ultrafiltration it is imperative to include the effect of variable viscosity in determining the polarization in crossflow systems. To do this accurately, it is necessary that the viscosity-concentration relationship is adequate to quite high concentrations.

Equations 8, 9 and 14 show clearly how the operating conditions and physical properties affect concentration polarization. Thus, polarization may be reduced by:

i) decreasing the inlet concentration which decreases the rate of change of μ_w^+, as indicated in Table 1. Equation 14, together with Eqs. 15–17, shows explicitly that the reduced downstream distance required for a given c_w^+ decreases exponentially as c_o increases in the expression for μ_w^+.

ii) the integral in Eq. 14 depends only on c_o for a given solution as indicated in Eqs. 15–17. Therefore, the arrangement of process variables and physical properties in the coefficient of the integral determine how these parameters affect the relationship between c_w^+ and the real reduced distance downstream, x/h. Therefore, decreasing the flux, increasing the diffusion coefficient and decreasing the spacing between membranes decrease the polarization for a given x/h.

The effectiveness of each of these measures in reducing polarization clearly is dependent on both the macromolecule involved and on the location of the operating point on Figure 1. For example, the asymptotic ξ value at which a "blow-up" in polarization occurs is approached much more rapidly for a solution with an inlet concentration of 5% wt. than for one of 1% wt., and for BSA these values of ξ are about 9 and 117. Hence, a reduction in

v_w near this value of ξ may have a much more dramatic effect on the 5% wt. solution than on the 1% wt. solution. In addition, because

$$\xi \propto \frac{x\, h\, v_w^3}{u_o} \tag{18}$$

it is obvious that changes in the permeate flux are likely to have a greater impact on the polarization than changes in channel length, height, or crossflow velocity.

The presence of an asymptotic value of ξ, at which there is a blowup of concentration polarization, and the fact that it varies with inlet concentration, highlights the necessity of optimizing the operating conditions for each module and solution encountered industrially and not relying on manufacturers' specifications which are often for systems vastly different from those of the user. Common practice is to operate well into the gel-polarized region and present results indicate that the effective channel length is severely reduced below that previously anticipated. This may prove to be extremely wasteful in terms of capital and/or operating costs and attention should be paid to designs which will reduce the gel formation problem.

Correct choice of conditions becomes even more important when dealing with species such as BSA which display severe fouling characteristics. Where a clear link can be established between a specific wall concentration and irreversible fouling, graphs such as those presented in Figure 1 could be used to select operating parameters which would minimize the fouling.

Accurate modelling of the polarization process, therefore, becomes of paramount importance. The present model is limited by several assumptions and the fact that the permeate flux (v_w) is considered to be constant. Thus, the data presented are qualitatively correct but the determination of their quantitative accuracy requires more computations. Work is in progress to produce a numerical solution for variable permeate flux which may be more appropriate for practical applications.

Notation

c = concentration, wt. %
$c^+ = c/c_o$
D = solute diffusivity, $m^2 \cdot s^{-1}$
$D^+ = D/D_o$
h = half channel height, m
Re = Reynolds number $h\, u_o/\nu_o$
u = cross-flow velocity, $m \cdot s^{-1}$
$u^+ = u/u_o$
v = permeate velocity, $m \cdot s^{-1}$
$v^+ = hv/\nu_o$
x = longitudinal distance, m
$x^+ = x/h\, Re$
x_1 = longitudinal distance function defined by Eq. 7
y = distance from center of channel, m
$y^+ = y/h$

Greek letters

μ = solution viscosity, pa $\cdot$ s
$\mu^+ = \mu/\mu_o$
ν = kinetic viscosity, $m^2 \cdot s^{-1}$
$\xi = 3(x/h)(v_w/u_o)(v_w h/D_o)^2$
$\xi_1 = 3(x_1/h)(v_w/u_o)(v_w h/D_o)^2$
ρ = solution density, $kg \cdot m^{-3}$

Subscripts

g = gel
m = membrane
o = inlet
p = permeate
s = solute
w = wall
x = longitudinal distance
y = transverse distance from membrane

Acknowledgment

The contribution to this research by W.N. Gill was supported in part by NSF Grants INT 85-13319 and 87-96330. Part of the contribution of W.N. Gill was made while he was a Fulbright Senior Research Scholar at the University of New South Wales in Australia.

Literature Cited

Bird, R. B., W. E. Steward, E. N. Lightfoot. *Transport Phenomena,* New York, Wiley (1960).

Blatt, E. F., A. Dravid, A. S. Michaels, and L. Nelson, "Solute Polarization and Cake Formation in Membrane Ultrafiltration: Causes, Consequences and Control Techniques," *Membrane Science and Technology,* J. E. Flinn, ed., New York, Plenum Press, 47 (1970).

Brian, P. L. T., "Concentration Polarization in Reverse Osmosis Desalination with Variable Flux and Incomplete Salt Rejection," *Ind. Eng. Chem. Fund.,* 4(4), 439 (1965).

Clifton, M. J., N. Abidine, P. Aptel, and Y. Sanchez, "Growth of the Polarization Layer in Ultrafiltration with Hollow-Fibre Membranes," *J. Memb. Sci.,* **21,** 233 (1984).

DeLuca, R., R. Shaw, and W. N. Gill, "Reverse Osmosis: Increased Productivity by Reduction of Concentration Polarization in Laminar Flow Reverse Osmosis Using Intermediate Non-Rejecting Membrane Sections," *Desalination,* **11,** 189 (1972).

Derzansky, L., and W. N. Gill, "The Mechanisms of Brine-Side Mass Transfer in a Horizontal Tubular Membrane," *AIChE J.,* **20,** 751 (1974).

Doshi, M. R., A. K. Dewan, and W. N. Gill, "The Effect of Concentration Dependent Viscosity and Diffusivity on Concentration Polarization in Reverse Osmosis Flow Systems," *AIChE Symp. Ser.,* **68,** 323 (1971).

Dresner, L., "Boundary Layer Build-Up in the Demineralization of Salt Water by Reverse Osmosis," Oak Ridge Nat. Lab., Report 3621 (May, 1964).

Fane, A. G., C. J. D. Fell, and A. G. Waters, "The Relationship Between Membrane Surface Pore Characteristics and Flux for Ultrafiltration Membranes," *J. Memb. Sci.,* **9,** 245 (1981).

Gill, W. N., C. Tien, and D. W. Zeh, "Analysis of Continuous Reverse Osmosis Systems for Desalination," *Int. J. Heat Mass Transf.,* **9,** 907 (1966).

Jonsson, G., "Boundary Layer Phenomena During Ultrafiltration of Dextran and Whey Protein Solutions," *Desalination,* **51**(1), 61 (1984).

Kozinski, A. A., and E. N. Lightfoot, "Ultrafiltration of Proteins in Stagnation Flow," *AIChE J.,* **17**(1), 81 (1971).

———, "Protein Ultrafiltration: A General Example of Boundary Layer Filtration," *AIChE J.,* **18**(5), 1030 (1972).

Porter, M. C., "Concentration Polarization with Membrane Ultrafiltration," *Ind. Eng. Chem. Prod. Res. Dev.,* **11**(3), 234 (1972).

Shen, J. J. S., and R. F. Probstein, "Ultrafiltration of Macromolecular Solutions," *Ind. Eng. Chem. Fund.,* **16,** 459 (1977).

Sherwood, T. K., P. L. T. Brian, and R. E. Fisher, "Salt Concentration at Phase Boundaries in Desalination Processes," M.I.T. Desalination Res. Lab., Report 295-1 (1963).

Sherwood, T. K., P. L. T. Brian, R. E. Fisher, and L. Dresner, "Salt Concentration at Phase Boundaries in Desalination by Reverse Osmosis," *Ind. Eng. Chem. Fund.,* **4**(2), 113 (1965).

Weast, R. C., *CRC Handbook of Chemistry and Physics,* 65th ed., CRC Press, Boca Raton (1985).

Wijmans, J. G., S. Nakao, and C. A. Smolders, "Flux Limitation Ultrafiltration: Osmotic Pressure and Gel Layer Model," *J. Memb. Sci.,* **20**(2), 115 (1984).

Manuscript received Dec. 29, 1987, and revision received May 9, 1988.