————., "Aqueous Solutions of Two or More Strong Electrolytes. Vapor Pressures and Solubilities," *Ind. Eng. Chem. Process Design Develop.*, **12**, 205 (1973).

Millero, F. J., "The Enthalpy of Seawater from 0 to 30°C and from 0 to 40% Salinity," *J. Marine Research*, **31**, 1 (1973).

NEL Steam Tables 1964, Her Majesty's Stationary Office, Edinburgh, Scotland.

Pitzer, K. S., "Thermodynamic Properties of Aqueous Solutions of Bivalent Sulfates," *J. Chem. Soc. Faraday Trans. II*, **68**, 101 (1972).

————., "Thermodynamics of Electrolytes, I. Theoretical Basis and General Equations," *J. Phys. Chem.*, **77**, 268 (1973).

————., and G. Mayorga, "Thermodynamics of Electrolytes, II. Activity and Osmotic Coefficients for Strong Electrolytes with one or both Ions Univalent," *ibid.*, **77**, 2300 (1973).

Ray, P., "Thermodynamic Properties of Sea Salt Solutions by Boiling Point Elevation Method," Ph.D. dissertation, Univ. California, Berkeley (1973).

Robinson, R. A., and R. H. Stokes, *Electrolyte Solutions*, 2nd Rev. Edit., Butterworths, London (1968).

Rush, R. M., and J. S. Johnson, "Osmotic Coefficients of Synthetic Sea Water Solutions at 25°C," *J. Chem. Eng. Data*, **11**, 590 (1966).

Singh, D., and L. A. Bromley, "Relative Enthalpies of Sea Salt Solutions at 0 to 75°C," *ibid.*, **18**, 174 (1973).

Spiegler, K. S., *Salt Water Purification*, Wiley, New York (1962).

Sridhar, S., "Boiling Point of Sea Salt Solutions," M.S. thesis, Univ. California, Berkeley (1970).

Stoughton, R. W., and M. H. Lietzke, "Calculation of Some Thermodynamic Properties of Sea Salt Solutions at Elevated Temperatures from Data on NaCl Solutions," *J. Chem. Eng. Data*, **10**, 254 (1965).

Stoughton, R. W., and M. H. Lietzke, "Thermodynamic Properties of Sea Salt Solutions," *ibid.*, **12**, 101 (1967).

Manuscript received August 28, 1973; revision received November 20 and accepted November 26, 1973.

Boundary-Layer Skimming: Calculational Curiosity or Promising Process?

It is suggested that the productivity of ultra-filtration and reverse osmosis can be increased substantially where the desired product is concentrated in the diffusional boundary layer adjacent to the membrane. This increase can be achieved by removing product preferentially from the boundary-layer region. The possible concentration increase and yield of such a skimming process are predicted to be very significant for the constant-property approximation and stagnation flow considered in this exploratory paper.

HO-LUN LEE and
E. N. LIGHTFOOT
Department of Chemical Engineering
University of Wisconsin
Madison, Wisconsin 53706

SCOPE

This paper suggests the possibility of substantially increasing the capacity of ultra-filtration equipment by skimming off the concentrated boundary layers which form adjacent to the filtration membrane. It builds on two previous papers from our laboratory (Kozinski et al., 1971, 1972) which are devoted to description of protein boundary layers, and on the generalized boundary-layer analysis of Stewart (1963).

The skimming process is described schematically in Figure 1, and a specific example, two-dimensional stagnation flow, is shown in Fig. 2. Behavior is described in terms of a concentration factor f and an effectiveness e defined by

$$f = c_{sk}/c_\infty \tag{1}$$

where c_{sk} is the cup-mixing concentration of solute in the skimmed layer and c_∞ is that in the approaching fluid, and

$$e = fQ_{sk}/(Q_{sk} + Q_{uf}) \tag{2}$$

where Q_{sk} is the volumetric rate at which the boundary layer is skimmed off, and Q_{uf} is the volumetric rate of ultrafiltration.

The effectiveness is just the ratio of (hypothetical) effective protein concentration in the solution removed, by a combination of ultra-filtration and skimming, to that outside the boundary layer. Its significance can perhaps be seen most clearly in a simple closed system operating continuously, as shown in Figure 3. For this situation

$$e = c_F/c_\infty \tag{3}$$

where c_F is feed concentration. Clearly $0 \leq e \leq 1$. The concentration factor on the other hand will always be greater than unity.

CONCLUSIONS AND SIGNIFICANCE

The results of this preliminary analysis, summarized in Figures 4 and 5, are very encouraging for concentration of solutes by boundary-layer skimming, in either ultra-filtration or reverse osmosis. Efficient fractionation based on differences in solute diffusivity also appear possible, but the picture here is less clear.

The effectiveness of boundary-layer skimming for solute concentration is shown in Figure 4. Here effectiveness e is plotted against the concentration factor f with the ratio of wall (membrane surface) concentration c_w to bulk concentration c_∞ as a parameter. As an example consider a 0.1% feed solution filtered at such a rate that wall concentration is 1.67%. This situation corresponds to the second curve from the right in the figure and represents a fairly modest filtration pressure. If skimming is conducted at such a rate that $f = 8.5$ we find that e is about 0.43 and f/e is 20. For the steady state batch system this means that product concentration is 20 times feed concentration whereas bulk concentration (equal to product concentration in the absence of skimming at the same filtration rate and bulk concentration) is only about $(1/0.43) = 2.32$ times feed concentration. Even more impressive results are predicted for higher filtration pressure.

This is the third in a series of papers from our laboratory exploring the potentialities of ultra-filtration for the concentration and separation of proteins and other high-molecular weight solutes.

In the first paper Kozinski and Lightfoot (1971) showed that the diffusional and hydrodynamic characteristics of protein boundary layers were primarily responsible for the observed limitations on equipment productivity. They also developed a simple and reasonably successful method for predicting equipment performance in the concentration of globular proteins, which requires no transport or thermodynamic data. In the second paper (1972) these same authors showed that much improved predictions could be obtained by using experimental viscometric and diffusional data, and by including osmotic effects. Thus they were able to obtain excellent agreement between prediction and experiment for filtration of bovine serum albumin solutions on a spinning-disk ultra-filter.

Admittedly solutions of native serum albumin are particularly well behaved and well characterized. It must also be kept in mind that proteins can denature under ultra-filtration conditions and produce much bigger resistance to water movement than would occur for the native proteins. This situation is probably common in commercial processes and was found by Kozinski and Lightfoot even for purified serum albumin at low ionic strength (1972). It does seem, however, that for practical engineering purposes the nature of boundary layers of pure native proteins, and their effects on the productivity of ultra-filtration equipment, are fairly well understood.

Analyses of the above type show that protein concentrations within the boundary layers are typically very much larger than in the bulk of the solution being filtered. Furthermore, even though these boundary layers can be thinned, as by using higher Reynolds numbers, the economics of ultra-filtration is such that they always impose a serious limitation on equipment performance.

It is thus of interest to determine if advantage may be taken of the boundary layers by preferentially withdrawing product from these regions of high solute concentration, that is, by boundary layer skimming.

Such a skimming process is indicated schematically in Figure 1 for the commercially interesting tubular or flat-plate geometries. The dashed lines represent the filtration membrane, permeable to water but not the excluded solute. The dotted lines represent the skimming ports. These may be simple slits, or perhaps such porous surfaces as sintered particulate plates, through which the boundary layers developed on the upstream membrane are removed. Multiple stages are shown here as equipment performance can be increased by using shorter boundary layers. In the simplest case, however, only a single stage would be used, and the primary advantage would be increased solute concentration in the product. The bulk solution leaving from such an apparatus can of course be recycled.

The effectiveness and concentration factor are dependent upon the thickness of the skimmed layer. This dependence is shown for e in Figure 5, which is for stagnation flow, in terms of the dimensionless skimming thickness

$$H = Y/\delta(X) \qquad (4)$$

where $\delta(X)$ is the boundary layer thickness. It can be seen that skimming is effective only when the layer's thickness is about δ.

Fractionation of solutes with different diffusivities can also be achieved by controlling the skimming rate, that is, the fraction of the boundary layer removed. This is possible because boundary layer thickness increases with an increase in diffusivity.

To determine the feasibility of such a process will ultimately require careful experimentation, and it is quite probable that substantial practical difficulties will be encountered in skimming off boundary layers with thicknesses of the order of microns. It is therefore desirable to assess process potentialities and to obtain a guide to any later experiments via a mathematical analysis. Such is the purpose of the present paper. To accomplish it we first obtain some general results from boundary layer theory, which is in a readily usable form for people interested in other geometries, and then treat as a specific example a system particularly simple to analyze: two-dimensional stagnation flow with negligible variation of viscosity, diffusivity, and osmotic pressure. This approach will be seen to permit description of a very wide range of conditions in a very compact way.

Stagnation flow is a convenient example because results are the same for all membrane lengths: the description is geometry independent. This is, however, also approximately true under commercially interesting conditions for

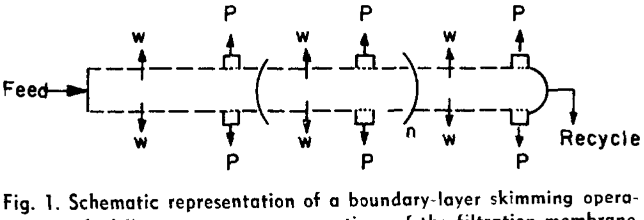

Fig. 1. Schematic representation of a boundary-layer skimming operation. Dashed lines represent cross-sections of the filtration membrane, and the dotted lines those of the skimming ports. The streams marked w are ultra-filtrate (essentially water in many cases) and those marked p are product streams (for example, concentrated protein solutions).

many other geometries of interest: No significant length enters into the final picture, and Equations (5) through (22) apply to all. Specialization to a specific geometry is required, as in Equation (23), when e/f is to be calculated. Behavior of more concentrated solutions requires consideration of property variations and will be discussed in a later paper.

THEORETICAL DEVELOPMENT

We will be concerned here with those systems for which the three-dimensional similarity transformation of Stewart (1963) is applicable. For these the concentration profile is given by[*]

$$\frac{d^2\Pi}{d\eta^2} = -\left(3\eta^2 + \frac{c_w - c_\infty}{c_w}\frac{d\Pi}{d\eta}\bigg|_{\eta=0}\right)\frac{d\Pi}{d\eta} \qquad (5)$$

with

$$\text{B.C. 1:} \quad \text{At} \quad \eta = 0 \quad \Pi = 0 \qquad (6)$$

$$\text{B.C. 2:} \quad \text{As} \quad \eta \rightarrow \infty \quad \Pi \rightarrow 1 \qquad (7)$$

Here

$$\Pi = \frac{c_i - c_w}{c_\infty - c_w} = \text{a dimensionless solute concentration}$$

$$\eta = y/\delta(x) = \text{relative distance into the boundary layer from the wall} \qquad (8)$$

The boundary layer thickness δ is given by

$$\delta = \frac{1}{\sqrt{\dot{\gamma} h_z}}\left(9\mathcal{D}_{iw}\int_0^x \sqrt{\dot{\gamma} h_z^3}\, h_x dx\right)^{1/3} \qquad (9)$$

$$\dot{\gamma} = \dot{\gamma}(x, z) = \left(\frac{\partial v_x}{\partial y}\bigg|_{y=0}\right) \qquad (10)$$

Here x and z are coordinates along the ultra-filtration surface, in the direction of and perpendicular to the immediately adjacent streamlines respectively, and y is distance from the surface measured along its local normal. The scale factors h_x and h_z are defined by

$$ds^2 = (h_x dx)^2 + (dy)^2 + (h_z dz)^2$$

where ds is the distance between two points separated by coordinate differences (dx, dy, dz). This coordinate system is described in detail by Stewart (1963). For two-dimensional systems, as considered in our example, h_x and h_z may be taken as unity. Then x is defined as actual distance along the surface in the direction of flow, and the z-coordinate need not be considered.

Equations (5) through (7) are applicable in the boundary-layer approximation to systems of arbitrary geometry, and this approximation is an excellent one for the high Schmidt numbers of interest to us here—especially for ultra-filtration.

They do, however, require that permeation velocity through the wall satisfy the relation:

$$-v_y\big|_{y=0} = \frac{\mathcal{D}_{iw}}{\delta}\,\frac{c_w - c_\infty}{c_w}\,\frac{d\Pi}{d\eta}\bigg|_{\eta=0} \qquad (11)$$

a restraint discussed briefly in Kozinski and Lightfoot (1972). Equation (11) will be satisfied identically for systems of position-independent boundary layer thickness: spinning disks and both two-dimensional and axi-symmetric stagnation flows. It will also be approximately valid for arbitrary geometry in the limit of high pressure drop across the membrane, which is characteristic of commercial ultra-filtrations. This situation corresponds to exactly one curve in our plots, that is, the curve with wall concentration c_w equal to the saturation concentration of the high-molecular weight solute. It follows that this is the curve of industrial interest. Equations (5) through (7) therefore provide an adequate description for a very large number of practical situations except of course for the neglect of property variations. Furthermore it is clear that the dimensionless profile $\Pi(\eta)$ depends only upon the parameter

$$\frac{c_w - c_\infty}{c_w}\Pi'(0) \equiv U \qquad (12)$$

for which we shall use the symbol U as indicated.

We may now calculate the ultra-filtration rate from Equation (11) and the skimming rates from the integral of Equations (5) through (7), which may be written formally as

$$\Pi = \frac{\int_0^\eta e^{-(p^3+pU)}dp}{\int_0^\infty e^{-(p^3+pU)}dp} = \Pi'(0)\int_0^\eta e^{-(p^3+pU)}dp \qquad (13)$$

where $\Pi'(0)$ is $d\Pi/d\eta|_{\eta=0}$. Our calculations are based on the integrals

$$Q_{\text{uf}} = \int_0^X\int_0^Z -v_y|_{y=0}\, h_x h_z\, dz dx \qquad (14\text{a})$$

$$= U\,\mathcal{D}_{iw}\int_0^X\int_0^Z h_x h_z \frac{dzdx}{\delta} \qquad (14\text{b})$$

$$Q_{\text{sk}} = \int_0^Y\int_0^Z h_z v_x\, dzdy \qquad (15\text{a})$$

$$= \frac{H^2}{2}\int_0^Z \dot{\gamma} h_z \delta^2 dz \qquad (15\text{b})$$

where $H = Y/\delta(X)$.

$$c_{\text{sk}} = \int_0^Y\int_0^Z h_z v_x c_i\, dzdy/Q_{\text{sk}} \qquad (16\text{a})$$

$$= c_w - (c_w - c_\infty)\cdot\frac{2}{H^2}\int_0^H \Pi\eta d\eta \qquad (16\text{b})$$

Here the filtration area is the region

$$0 < x < X;\ 0 < z < Z \qquad (17)$$

and the skimmed zone extends from

$$0 < \eta < H \qquad (18)$$

Relations (17) could be further generalized if desired, but those given are sufficient for our present purposes.

We are now in a position to determine the functions f and e for any given permeation rate and thickness of layer skimmed. For these purposes it is convenient to begin by selecting convenient values of U and then proceeding as follows:

1. Calculate c_w/c_∞ from Equation (12) and the chosen value of U:

$$\frac{c_w}{c_\infty} = \left(1 - U\int_0^\infty e^{-(p^3+Up)}dp\right)^{-1} \qquad (19)$$

This integral is simply evaluated numerically.

---

[*] The essentially simple nature of such systems is discussed by Lightfoot (1969), p. 41, for the simpler case of an impermeable wall and by Kozinski et al. (1972) for ultra-filtration. These references and Acrivos (1962) may provide useful background.

2. Calculate f from Equations (16b) and (19):

$$f = \frac{c_{sk}}{c_\infty} = \frac{c_w}{c_\infty} - \left(\frac{c_w}{c_\infty} - 1\right)\frac{2}{H^2} I \qquad (20)$$

where the integral $I = \int_0^H \Pi\eta d\eta$ may be most conveniently obtained by changing the original order of integration and then integrating by parts. One thus obtains

$$f = \frac{c_w}{c_\infty}\left\{1 - \frac{U}{H^2}\left[\frac{1}{3}\left(e^{-(H^2+UH)} - 1\right) + \left(H^2 + \frac{U}{3}\right)\int_0^H e^{-(p^3+pU)}dp\right]\right\} \qquad (21)$$

This integral may be evaluated in essentially the same way as that in Equation (19), thus simplifying the calculation procedures. Note that this result is completely geometry independent and most particularly that it does not depend upon the size of the ultra-filtration zone.

3. Calculate (e/f) from the relation:

$$\frac{e}{f} = \frac{\frac{H^2}{2}\int_0^Z \dot\gamma(h_z\delta^2)\,dz}{\frac{H^2}{2}\int_0^Z \dot\gamma(h_z\delta^2)\,dz + U\,\mathfrak{D}_{iw}\int_0^X\int_0^Z \frac{h_x h_z dz dx}{\delta}} \qquad (22)$$

It may be noted that all geometry dependence occurs here and furthermore that e/f depends only upon geometry (including the thickness of the skimmed layer).

The integrals of Equation (22) may be simply evaluated for many situations, but for illustrative purposes we consider here the special case of two-dimensional and axi-symmetric flows [see, for example, Acrivos (1962)]. For these h_z and δ are independent of z, and h_x may be taken as unity. We may thus write

$$\frac{e}{f} = \left[1 + \frac{2U\,\mathfrak{D}_{iw}}{H^2\delta(X)^2\dot\gamma(X)h_z(X)}\int_0^X \frac{h_z(x)}{\delta(x)}dx\right]^{-1} \qquad (23)$$

(two-dimensional or axi-symmetric)

For two-dimensional systems h_z is also unity, and Equation (22) simplifies still further.

APPLICATION OF THE THEORY

We consider here as a particularly simple example the two-dimensional stagnation flow of Figure 2. For it we may use Equation (23) with h_z equal to unity and furthermore write [see, for example, Batchelor (1967)]:

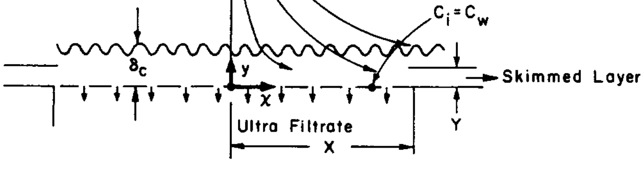

Fig. 2. Skimming in stagnation flow. Solution of concentration c_x approaches a flat wall at high Reynolds number to produce a concentration boundary layer, which for this situation has a uniform thickness δ_C. The filtration membrane extends a distance X in the direction of flow from the stagnation locus and at $x = X$ a layer of thickness Y is removed in such a way as not to disturb the upstream flow.

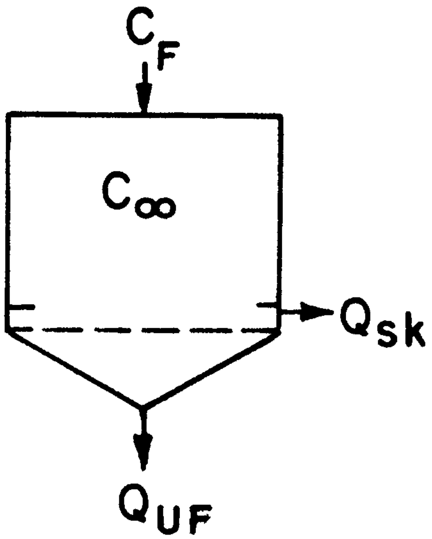

Fig. 3. A simple continuous ultra-filtration system.

$$\dot\gamma = \alpha x \quad \text{and} \quad \alpha = F''(0)\,k\sqrt{k/\nu} \qquad (24)$$

where k is a measure of the strength of the flow and $F''(0)$ is a tabulated constant. From Equation (9),

$$\delta^3 = \frac{9\mathfrak{D}_{iw}}{(\alpha X)^{3/2}}\int_0^X (\alpha x)^{1/2}dx = 6\mathfrak{D}_{iw}/\alpha \qquad (25)$$

$$\frac{e}{f} = \left[1 + \frac{1}{3}\frac{U}{H^2}\right]^{-1} \qquad (26)$$

With f known from Equation (21), e can be calculated from Equation (26). Figures 4 and 5 are constructed from these relations by straightforward mathematical operations. These figures are centers of the discussion which follows.

DISCUSSION

The effectiveness-concentration relations shown in Figure 4 are the most important result of the above analysis. It is suggested here that successful skimming could increase product concentration manyfold without change in filtration rate. Furthermore, though these results are specific for two-dimensional stagnation flow, there is no reason to expect a marked dependence on geometry. The effect of the thickness of the skimmed layer on skimming effectiveness, shown in Figure 5, also suggests that skimming may prove feasible as a means of fractionation. There are, however, a number of questions yet to be resolved.

The significance of Figure 4 can perhaps be most easily seen for the conditions of Figure 3 by noting that f/e is the predicted ratio of product to feed concentration in a skimming operation while the corresponding ratio without skimming is $1/e$. One can easily compare these quantities for any degree of polarization (c_w/c_∞) shown in the figure, as indicated by the numerical example in Conclusions and Significance. It can readily be seen that both high product concentration and effectiveness are predicted at even rather modest levels of polarization. Similar conclusions can be obtained from a recent paper by Gill et al. (1972) written from a different point of view.

The dependence of effectiveness and concentration factor on thickness of skimmed layer shown in Figure 5 can be used as a basis for fractionation. For any given filtration rate c_w/c_∞ will be less for a higher solute diffusivity

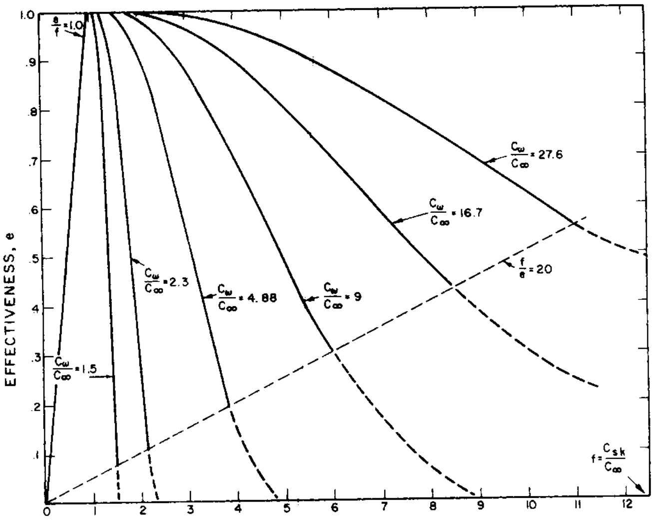

Fig. 4. Plot of equipment effectiveness vs. concentration by skimming.

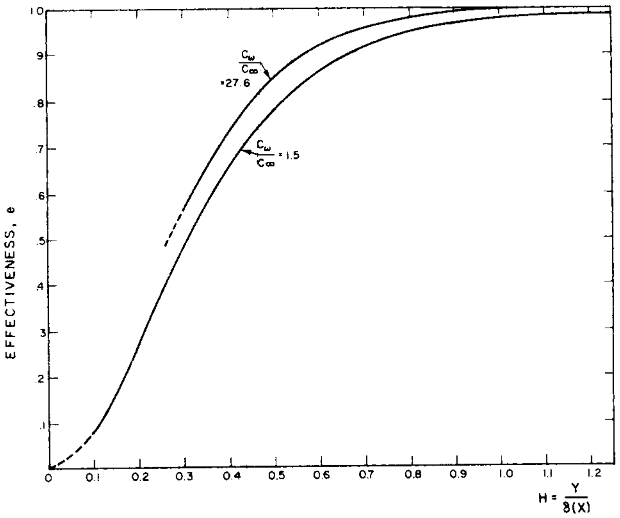

Fig. 5. Plot of effectiveness vs. fraction of boundary layer thickness from membrane surface $H = \dfrac{Y}{\delta(X)}$.

and boundary layer thickness will increase [Equation (11)]. Effectiveness will then tend to decrease with increased diffusivity, and the difference in effectiveness for any two solutes can be maximized by proper choice of filtration rate (through its effect on c_w/c_∞) and H. The change of e with c_w/c_∞ and H is sufficiently large at low e that efficient separations seem possible even though boundary-layer thickness only varies with the 1/3-power of solute diffusivity. However, both the concentration dependence of transport properties and solute-solute interactions in the boundary layer may influence separability very substantially. A more thorough analysis of solute separation is therefore in order.

We have already prepared some preliminary calculations for variable-property systems, and these can be easily extended. They show diminished effectiveness of skimming as expected, but they are still quite encouraging.

There seems no doubt that successful skimming would be highly beneficial, particularly in raising permissible product concentrations for systems of high viscosity. The main uncertainties are as to the mechanical feasibility of this process and its comparison with alternate means for achieving similar ends, for example, use of hollow fibers. We hope to work on these aspects of the problem next.

NOTATION

c_i = concentration of species i
c_F = feed concentration of i
c_{sk} = skimming-product concentration of i
c_w = concentration of i at membrane surface
c_∞ = bulk concentration
$\mathcal{D}_{iw}$ = pseudo-binary diffusion coefficient of species i in water
e = effectiveness factor as defined in Equation (2)
f = concentration factor defined in Equation (1)
$F(y)$ = function given in Batchelor (1967) showing y-dependency of x-component velocity
h = scale factors for any set of three-dimensional curvilinear coordinates
H = ratio of skimmed layer's thickness to boundary layer thickness δ
I = an integral, $\int_0^H \Pi\eta\, d\eta$
k = strength of flow for the stagnation flow considered
p = dummy integral variable
Q_{sk} = skimming product's flow rate
Q_{uf} = ultra-filtration rate
s = distance of point from origin
U = dimensionless parameter defined by Equation (12)
v_x = x-component of velocity
v_y = y-component of velocity
x = curvilinear coordinate
X = x-dimension of system
y = curvilinear coordinate
Y = thickness of skimmed layer
z = curvilinear coordinate
Z = z-dimension of system

Greek Letters

α = proportionality constant between surface shear rate and distance in x
$\dot{\gamma}$ = shear rate at membrane surface
δ = concentration boundary thickness, as defined by Equation (9)
η = ratio of actual distance from surface to boundary layer thickness
Π = dimensionless concentration

LITERATURE CITED

Acrivos, A., "On the Solution of the Convection Equation in Boundary-Layer Flows," *Chem. Eng. Sci.*, **17**, 457 (1962).

Batchelor, G. K., *Fluid Dynamics*, Cambridge Univ. Press, England, p. 285 (1967).

Shaw, R. A., R. Deluca, 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).

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

————, "Protein Ultra-filtration: A General Example of Boundary Layer Filtration," *ibid.*, **1,8** 1030 (1972).

Lightfoot, E. N., "Estimation of Heat and Mass Transfer Rates," in *Lectures on Transport Phenomena*, R. B. Bird, et al., A.I.Ch.E. Continuing Educ. Ser. No. 4 (1969).

Stewart, W. E., "Forced Convection in Three-Dimensional Flows. I. Asymptotic Solutions for Fixed Surfaces," *AIChE J.*, **9**, 528 (1963).

Manuscript received July 2, 1973; revision received November 6 and November 8, 1973.