COMMUNICATIONS TO THE EDITOR

Effect of Longitudinal Diffusion in Reverse Osmosis

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Longitudinal diffusion has only a second-order, and often negligible, effect on membrane performance in the reverse osmosis process. This paper presents the equations governing the effect of longitudinal diffusion in specified reverse osmosis systems.

REVERSE OSMOSIS SYSTEM SPECIFICATION

A Loeb-Sourirajan type porous cellulose acetate membrane can be specified at any operating pressure in terms of its pure water permeability constant A, and the solute transport parameter $(D_{AM}/K\delta)$ at that pressure (*1*). A reverse osmosis system can be specified in terms of the dimensionless parameters γ, θ, and λ defined in terms of A, $(D_{AM}/K\delta)$, and the mass transfer coefficient k on the high pressure side of the membrane as follows (*2*):

$$\gamma = \frac{\pi(X_{A1}{}^0)}{P} \tag{1}$$

$$\theta = \frac{(D_{AM}/K\delta)}{v_w{}^*} \tag{2}$$

$$\lambda = \frac{k}{(D_{AM}/K\delta)} \tag{3}$$

All the symbols used are listed and defined at the end of the paper.

ASSUMPTIONS

As before (*2*), it is assumed that $(D_{AM}/K\delta)$ for the solute at a given operating pressure is independent of feed concentration and feed flow rate, the osmotic pressure of the feed solution is proportional to the mole fraction of solute, and the molar density of the solution is essentially constant.

BASIC TRANSPORT EQUATIONS

The following equations have been derived (*2* to *4*). For all values of γ, θ, and λ,

$$V_w = \frac{v_w}{v_w{}^*} = 1 - \gamma\,(C_2 - C_3) = \frac{\theta}{(\gamma C_3 + \theta)} \tag{4}$$

$$C_1 = C_3 \left[1 + \frac{1}{(\gamma C_3 + \theta)} \exp\left\{ - \frac{1}{\lambda(\gamma C_3 + \theta)} \right\} \right] \tag{5}$$

$$C_2 = \left[1 + \frac{1}{(\gamma C_3 + \theta)} \right] C_3 \tag{6}$$

$$C_2{}^0 = \left[1 + \frac{1}{(\gamma C_3{}^0 + \theta)} \right] C_3{}^0 \tag{7}$$

$$C_3 = \frac{\sqrt{(1 + \theta - \gamma C_2)^2 + 4\gamma\theta C_2} - (1 + \theta - \gamma C_2)}{2\gamma} \tag{8}$$

$$C_3{}^0 = \frac{\sqrt{(1 + \theta - \gamma C_2{}^0)^2 + 4\gamma\theta C_2{}^0} - (1 + \theta - \gamma C_2{}^0)}{2\gamma} \tag{9}$$

$$C_1(1 - \Delta) + \overline{C}_3\Delta = 1 \tag{10}$$

where

$$\Delta = 1 - \frac{\overline{u}}{\overline{u}^0} = \text{fraction product recovery} \tag{11}$$

assuming cross-sectional area for fluid flow. Equations (4) to (9) are applicable at any point in the reverse osmosis system, and Equation (10) is simply a material balance equation for any section of the reverse osmosis unit; they are applicable for any reverse osmosis system whether or not longitudinal diffusion is negligible.

The performance data which are of basic interest in any reverse osmosis unit are C_1, C_2, C_3, $\overline{C}_3$, and Δ as functions of the longitudinal distance parameter X defined as

$$X = \frac{v_w{}^*}{\overline{u}^0} \frac{x}{h} \tag{12}$$

If any two of the five quantities C_1, C_2, C_3, $\overline{C}_3$, and Δ are available, the other three can be calculated simply by the use of Equations (4) to (10).

OTHER PARAMETERS NEEDED FOR ANALYSIS

Two other parameters are needed for the present analysis, one involving the longitudinal length L over which mixing is considered, and the other involving the longitudinal diffusion coefficient E which is assumed constant. These two parameters are expressed here as M and PeB respectively defined as follows:

$$M = \frac{h}{v_w{}^*} \frac{\overline{u}^0}{L} \tag{13}$$

$$PeB = \frac{\overline{u}^0 L}{E} \tag{14}$$

In any practical case, by fixing L, M is fixed; further, since $XM = x/L$, $XM = 0$ at fluid inlet, and $XM = 1$ at fluid exit.

With the present state of knowledge of the reverse osmosis process, no definite statement can be made on the value of E to be used in any practical case. If only the applicable value of E, and hence PeB, is known, its effect on membrane performance can be predicted exactly on the basis of the following analysis.

LONGITUDINAL MIXING—GENERAL CASE

From material balance considerations, the following equations can be derived:

$$-E\frac{d^2C_1}{dx^2} + \overline{u}\frac{dC_1}{dx} = -\,(C_1 - C_3)\frac{d\overline{u}}{dx} \tag{15}$$

$$-\frac{d\overline{u}}{dx} = \frac{v_w}{h} = \frac{v_w{}^*}{h}\,[1 - \gamma(C_2 - C_3)] \tag{16}$$

Changing the variables, Equations (15) and (16) can be written as

$$-\frac{d^2C_1}{d(XM)^2} + PeB\,\overline{U}\frac{dC_1}{d(XM)} = -\,PeB\,(C_1 - C_3)\frac{d\overline{U}}{d(XM)} \tag{17}$$

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$$-\frac{d\bar{U}}{d(XM)} = \frac{\theta}{M(\gamma C_3 + \theta)} \tag{18}$$

where

$$\bar{U} = \frac{\bar{u}}{\bar{u}^0} \tag{19}$$

On integration, Equation (18) becomes

$$\bar{U} = 1 - \int_0^{XM} \frac{\theta}{(\gamma C_3 + \theta)} \frac{d(XM)}{M} \tag{20}$$

The boundary conditions of Equation (17) are:
at

$$XM = 0 \text{ (fluid inlet)}, -\frac{dC_1}{d(XM)} = PeB\,(1 - C_1) \tag{21}$$

at

$$XM = 1 \text{ (fluid exit)}, -\frac{dC_1}{d(XM)} = 0 \tag{22}$$

Equation (17) is nonlinear, and it can be solved numerically on a computer by the Milne method of integration (5). Thus the solution to Equation (17) gives the values of C_1 and (XM) for specified values of PeB and M for any reverse osmosis system; the corresponding Δ, C_3, and $\bar{C}_3$ values can be obtained from Equations (20), (5), and (10) respectively. Two sets of results of such calculations are illustrated in Figures 1 and 2 for the reverse osmosis system specified by the parameters $\gamma = 0.1$, $\theta = 0.001$, and $\lambda\theta = 1.0$.

Figure 1 gives the X vs. C_1 correlation for various values of PeB; this figure illustrates the effect of longitudinal diffusion on the values of C_1 from the inlet to the exit of the operating unit under consideration. Figure 2 illustrates $X(= 1/M)$ vs. C_1, $\bar{C}_3$, and Δ correlations as functions of PeB; the results given in this figure correspond to the exit condition $(XM = 1)$ and not for a fixed value of M.

The results of similar calculations for the reverse osmosis systems specified by the parameters $\gamma = 0$ to 0.5, $\theta = 0.001$ to 0.1, and $\lambda\theta = 1$ and ∞, show that up to $X(= 1/M) \approx 0.5$, C_1, $\bar{C}_3$, and Δ values are not very much affected by longitudinal diffusion.

LIMITING CASES

The limiting cases of $PeB \rightarrow \infty$, and $PeB = 0$ correspond respectively to zero longitudinal mixing, and complete longitudinal mixing respectively. No knowledge about the value of E is needed to study these cases. The former case has been extensively studied for desalination application (6); in a similar manner, the latter case can be studied for any reverse osmosis application using Equation (17) with the appropriate boundary condition, along with Equations (4) to (11), and (20).

CONCLUSION

The foregoing analysis presents the parameters and equations governing the effect of longitudinal diffusion in reverse osmosis. Together with the analysis presented earlier (2), it offers a unified approach to reverse osmosis process design as a unit operation in chemical engineering.

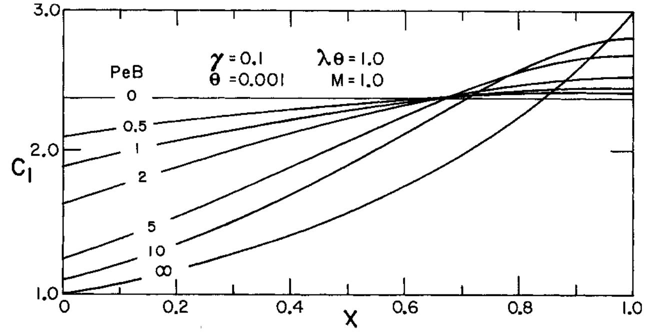

Fig. 1. Effect of longitudinal diffusion on C_1 from inlet to exit of operating unit.

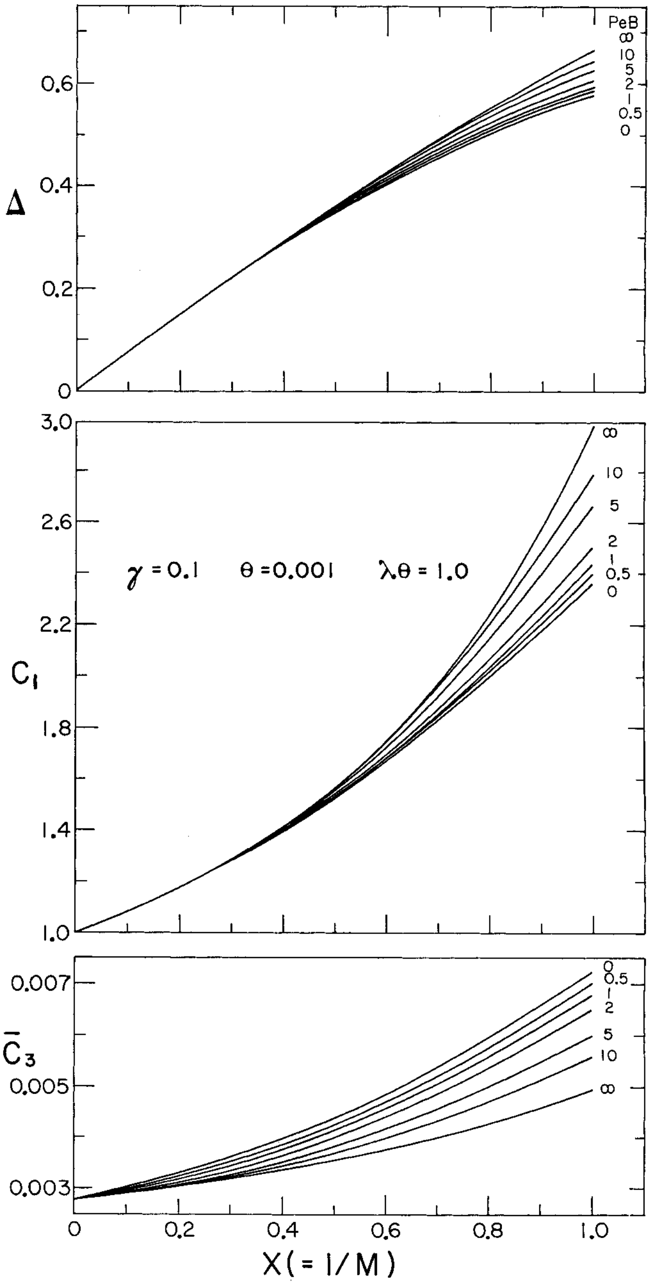

Fig. 2. X $(= 1/M)$ vs. $\bar{C}_3$, C_1, and Δ as functions of PeB for a specified reverse osmosis system.

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NOTATION

A = pure water permeability constant, g.mole water/(sq.cm.) (sec.) (atm.)
C = $c_A/c_{A1}{}^0$ or $X_A/X_{A1}{}^0$
$\bar{C}$ = $\bar{c}_A/c_{A1}{}^0$ or $\bar{X}_A/\bar{X}_{A1}{}^0$
c = molar density of solution, g.mole/cc.
c_A = molar concentration of solute, g.mole/cc.
$\bar{c}_A$ = average molar concentration of solute g.mole/cc.
$(D_{AM}/K\delta)$ = solute transport parameter, cm./sec.
E = longitudinal diffusion coefficient, sq.cm./sec.
$(1/h)$ = area of membrane surface per unit volume of fluid space, cm.$^{-1}$

k = mass transfer coefficient on the high pressure side of the membrane, cm./sec.
L = longitudinal length over which mixing is considered, cm.
M = quantity defined by Equation (13)
P = operating pressure, atm.
PeB = quantity defined by Equation (14)
$\overline{U}$ = $\overline{u}/\overline{u}^0$
$\overline{u}$ = average fluid velocity in the transverse length of the channel at a given x, cm./sec.
V_w = v_w/v_w^*
v_w = fluid velocity component in the direction perpendicular to the membrane surface, cm./sec.
v_w^* = AP/c, cm./sec.
X = quantity defined by Equation (12)
X_A = mole fraction of solute
$\overline{X}_A$ = average mole fraction of solute
x = longitudinal distance from chemical entrance, cm.

Greek Letters

γ = quantity defined by Equation (1)
Δ = quantity defined by Equation (11)
θ = quantity defined by Equation (2)
λ = quantity defined by Equation (3)
$\pi(X_A)$ = osmotic pressure corresponding to X_A, atm.

Subscripts

1 = bulk solution
2 = concentrated boundary solution
3 = membrane permeated product solution

Superscript

0 = condition at channel entrance

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Optimal Design of Jacketed Tubular Reactor with Taylor Diffusion

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For plug flow tubular reactors, steady state ideal optimal temperature policies for various reaction schemes are available [for example, (1 to 5)]. In the physical implementation, such perfect ideal policies provide theoretical upper bounds and may not exactly be achieved due to the nonideal flow behavior and the physical limitations in design and operation. The nonlinear behavior can be explained by Taylor diffusion and various engineering problems with such diffusion have been posed and solved in the past for isothermal and few nonisothermal tubular reactors (7 to 17). Isothermal reactors in particular have received attention and the effect of axial diffusion on the yield was studied (13, 14, 16). The ideal optimal temperature profile was also obtained for an ideal tubular reactor (14). The treatment of optimal heat flux in a tubular reactor with radial diffusion is available (18). The physical limitations in design and operation, on the other hand, are severe if the reactions are exothermic or endothermic. Under these circumstances, optimal jacketed tubular reactors may be used (6). This mode of configuration introduces additional constraints on the energy balance and leads in some cases to the reduction of an infinite dimensional optimization problem to a finite dimensional one.

JACKETED TUBULAR REACTOR WITH DIFFUSION

A steady state jacketed tubular reactor with Taylor diffusion in which $(n - 1)$ independent chemical species are involved in r independent reactions can be described by a system of n differential equations:

$$D_i \frac{d^2 v_i}{dz^2} - \nu \frac{dv_i}{dz} + \frac{\delta_{in}}{\alpha}[u - v_n] + f_i(k_1, \ldots, k_r, v_1, \ldots, v_n) = 0 \qquad (1)$$

$$(i = 1, 2, \ldots, n)$$

where the nth equation represents the energy balance of the reacting fluid. Here the jacket side coolant flow rate is assumed to be sufficiently large so that the variation in jacket temperature u along z is negligible. The boundary conditions at the entrance and the exit of the reactor are given by (7 to 10)

$$\nu v_{i0} = \nu v_i - D_i \frac{dv_i}{dz} \qquad \text{at} \quad z = 0 \qquad (2)$$

and

$$\frac{dv_i}{dz} = 0 \qquad \text{at} \quad z = L \qquad (3)$$

The rate constants are all assumed to follow Arrhenius' expression

$$k_j = k_{j0} \exp[-E_j/(R \cdot v_n)] \qquad (j = 1, 2, \ldots, r)$$

For a given chemical feed, it is to design the reactor optimally in some well posed sense. An objective function may be given. Then the optimization has to be carried out over the open variables. These are L and α in design and ν, u, and v_{n0} in operation. Among these variables, α and u appear only in the process equation, ν in both process equations and boundary conditions, v_{n0} in the boundary conditions, and L implicitly in the choice of ν. Since $\alpha = [r \cdot C_p \cdot \rho/(2 \cdot U)]$ and U is approximately proportional to $(\nu^{1/3}/r)$ for laminar flow and to $(\nu^{0.8}/r)$ for turbulent flow in a tube, α is proportional to $(r^2/\nu^{1/3})$ for laminar and to $(r^2/\nu^{0.8})$ for turbulent flow, respectively. Therefore if C_p and ρ do not change appreciably along z then for a given ν, α depends only on the choice of r and is constant along z. Consequently, the choice of α corresponds to fixing the radius. If the values for some of these variables are specified, then the optimization may be carried out for the remaining open variables. For this nonlinear two point boundary value problem, an analytical solution is not in sight and the solution technique is invariably a numerical one. However, the numerical technique poses some difficulty for this type of problem [for example, (15, 19, 20 to 22, 24)]. One of the efficient techniques that give a short computing time and a stable iterative computation

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