Some General Equations for Reverse Osmosis Process Design

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A generalized approach to reverse osmosis process design is presented for solution-membrane-operating systems characterized by the dimensionless parameters γ, θ, and λ defined in terms of the pure water permeability constant A, solute transport parameter ($D_{AM}/K\delta$), mass transfer coefficient k on the high pressure side of the membrane, and the properties of the solution. Analytical expressions are derived, in terms of dimensionless quantities, for the change of volume of solution, concentration of the bulk solution and that of the concentrated boundary solution on the high pressure side of the membrane, the change in the permeating velocity of solvent water through the membrane, solute separation, and the other related quantities, at any instance, as a function of concentration of the product solution on the atmospheric pressure side of the membrane, or time from the start of the operation for reverse osmosis systems specified by γ, θ, and λ. The equations are applicable to membranes for which ($D_{AM}/K\delta$) is independent of solute concentration and feed flow rate, and for aqueous feed solutions whose molar density can be assumed constant and whose osmotic pressure is proportional to mole fraction. The equations are developed first for the case of batch-by-batch operation, and their applicability to the flow case is then indicated.

Transport processes occurring across synthetic and natural membranes separating different solutions are of theoretical and practical interest. Before desalination by reverse osmosis became popular, almost the entire work on the subject was done by biologists. The permeability constants of natural membranes to water and solute were measured by many workers (*1, 2, 8, 9, 12, 16, 17*). Jacobs and Stewart (*16*) expressed the solute permeability constant as D_{AM}/δ, and Eyring and co-workers (*18*), who based their results on the theory of absolute reaction rates, expressed it as ($D_{AM}/K\delta$). After the invention of the Loeb-Sourirajan type porous cellulose acetate membranes (*10*), several studies have been reported on the transport of various solutes through such membranes (*3* to *5, 11, 14*). Lonsdale, et al. (*11*) proposed a homogeneous diffusion model for solute transport through the above membranes; their model also expresses solute permeability coefficient by a term equivalent to ($D_{AM}/K\delta$) (*13*). Transport equations based on nonequilibrium thermodynamics are given by several authors (*4, 13, 15*). Assuming constancy of three coefficients, namely the specific hydraulic permeability, the local solute permeability, and the reflection factor (which is said to be a quantitative index of solute separation), Spiegler and Kedem (*15*) have given transport equations theoretically applicable for the entire 0 to 100% range of solute separations, and their validity have been demonstrated experimentally by Jagur-Grodzinski and Kedem (*3*). However, the equations based on irreversible thermodynamics do not appear very convenient for reverse osmosis process design purposes.

The Kimura-Sourirajan analysis of the experimental reverse osmosis data offers a convenient approach for setting up general equations for reverse osmosis process design (*5, 14*). In this analysis, which is also applicable for the entire range of solute separations, the transport of water and solute through the membrane is specified by the pure water permeability constant A, and the solute transport parameter ($D_{AM}/K\delta$) which is independent of feed concentration and feed flow rate for several solution systems such as sodium chloride-water, glycerol-water, and urea-water. Provided the mass transfer coefficient k on the high pressure side of the membrane is available, or can be calculated, the quantities A, ($D_{AM}/K\delta$), and k enable the prediction of membrane performance for different operating conditions of feed concentration and feed flow rate at a given operating pressure (*14*). Thus the Kimura-Sourirajan analysis offers a rational basis for reverse osmosis process design based on the fundamental equations for solvent and solute transport through membranes; the process design procedure based on such analysis has beeen illustrated with particular reference to saline water conversion (*7*). This paper presents a generalized approach to reverse osmosis process design for solution-membrane-operating systems characterized by the dimensionless parameters γ, θ, and λ defined in terms of A, ($D_{AM}/K\delta$), k, and the properties of the feed solution (*6*). The equations presented in this paper are applicable to both natural and synthetic membranes for which ($D_{AM}/K\delta$) is independent of solute concentration and feed flow rate, and for aqueous feed solutions whose molar density may be assumed constant, and whose osmotic pressure is proportional to mole fraction of solute. The equations are developed first for the case of batch-by-batch reverse osmosis operation, and their applicability to the flow case is then indicated.

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DEFINITIONS

The solution-membrane-operating system is specified by the fundamental design parameters γ, θ, and λ defined as follows:

$$\gamma = \frac{BX_{A1}^0}{P} = \frac{B}{cP} c_{A1}^0 = \frac{B'}{P} c_{A1}^0 \tag{1}$$

$$\theta = \frac{c}{AP}\left(\frac{D_{AM}}{K\delta}\right) \tag{2}$$

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

In addition, the osmotic pressure-concentration relationships, the velocities of pure water and solvent water through the membrane, and the dimensionless solute concentrations are defined as follows for convenience in analysis:

$$\pi(X_A) = B\,X_A = B\frac{c_A}{c} = B'\,c_A \tag{4}$$

where B and B' are constants, and

$$\gamma^* = \frac{B}{cP} = \frac{B'}{P} \tag{5}$$

$$v_w{}^* = \frac{AP}{c} \tag{6}$$

$$v_w = \frac{N_B}{c} \tag{7}$$

$$C = \frac{c_A}{c_{A1}{}^0} \tag{8}$$

$$\frac{C_3}{C_3{}^0} = \frac{c_{A3}}{c_{A3}{}^0} = \phi_3 \tag{9}$$

Combining Equations (1) and (5)

$$\gamma = \gamma^*\,c_{A1}{}^0 \tag{10}$$

and

$$\gamma^*\,c_{A3} = \gamma\,C_3 \tag{11}$$

Combining Equations (2) and (6)

$$\theta = \frac{(D_{AM}/K\delta)}{v_w{}^*} \tag{12}$$

All the symbols used are listed and defined at the end of the paper. The subscripts 1 and 2 refer to the bulk solution and the concentrated boundary solution respectively on the high pressure side of the membrane, and the subscript 3 refers to the membrane permeated product solution. The superscript zero refers to the initial condition in the batch process or to the condition at membrane entrance in the flow process.

BASIC EQUATIONS

The following basic equations have been derived (*6*, *7*):

$$v_w = \frac{N_B}{c} = v_w{}^*\,[1 - \gamma(C_2 - C_3)] \tag{13}$$

$$C_1 = C_3\,q \tag{14}$$

where

$$q = 1 + \frac{1}{(\gamma C_3 + \theta)} \exp\left[-\frac{1}{\lambda(\gamma C_3 + \theta)}\right] \tag{15}$$

$$C_2 = \left[1 + \frac{1}{(\gamma C_3 + \theta)}\right] C_3 \tag{16}$$

$$C_3 = \frac{\sqrt{(1 + \theta - \gamma C_2)^2 + 4\gamma\theta C_2} - (1 + \theta - \gamma C_2)}{2\gamma} \tag{17}$$

Equations (13) to (17) are applicable at any point on the membrane surface at any time in the reverse osmosis separation system.

ANALYSIS OF BATCH-BY-BATCH REVERSE OSMOSIS PROCESS

The object of this analysis is to obtain analytical expressions, in terms of dimensionless quantities, for the change of volume of solution on the high pressure side of the membrane ($V_1/V_1{}^0$), the concentration of the bulk solution (C_1) and that of the concentrated boundary solution (C_2) on the high pressure side of the membrane, the change in the permeating velocity of water through the membrane ($v_w/v_w{}^0$), solute separation, and the other related quantities, at any instance, as a function of the concentration of the product solution (C_3) on the atmospheric pressure side of the membrane, or time from the start of the operation, for solution-membrane-operating systems specified by the parameters γ, θ, and λ.

General Case

At any time t, let V_1 and C_1 be the volume and concentration respectively of the bulk solution on the high pressure side of the membrane, and let V_3 and C_3 be the corresponding values for the membrane permeated product solution on the atmospheric pressure side of the membrane. At time $t = 0$,

$$C_1 = C_1{}^0 = 1 \tag{18}$$

$$C_3 = C_3{}^0 \tag{19}$$

$$V_1 = V_1{}^0 \tag{20}$$

At any time t,

$$-\,dV_1 = dV_3 \tag{21}$$

$$-\,d(V_1C_1) = C_3dV_3 = -\,C_3dV_1 \tag{22}$$

$$\therefore \frac{dV_1}{V_1} = -\frac{dC_1}{C_1 - C_3} \tag{23}$$

Integrating Equation (23),

$$\ln\frac{V_1}{V_1{}^0} = -\int_1^{C_1} \frac{dC_1}{C_1 - C_3} = -Z \tag{24}$$

where

$$Z = \int_1^{C_1} \frac{dC_1}{C_1 - C_3} \tag{25}$$

From Equation (14),

$$C_1 - C_3 = C_3(q - 1) \tag{26}$$

Differentiating Equations (14) and (15), and using Equation (26), Z may be expressed as

$$Z = \int_{C_3{}^0}^{C_3} \left[\frac{\gamma}{\lambda(\gamma C_3 + \theta)^2} - \frac{\gamma}{(\gamma C_3 + \theta)} + \left\{\frac{(\gamma C_3 + \theta)}{C_3} \exp\frac{1}{\lambda(\gamma C_3 + \theta)}\right\} + \frac{1}{C_3}\right] dC_3 \tag{27}$$

On integration Equation (27) becomes

$$\begin{aligned} Z = &-\frac{1}{\lambda}\left[\frac{1}{(\gamma C_3 + \theta)} - \frac{1}{(\gamma C_3{}^0 + \theta)}\right] \\ &- \left(1 + \theta e^{\frac{1}{\lambda\theta}} - \frac{1}{\lambda} - \theta\right) \ln\frac{(\gamma C_3 + \theta)}{(\gamma C_3{}^0 + \theta)} \\ &+ \left(1 + \theta e^{\frac{1}{\lambda\theta}}\right) \ln\frac{C_3}{C_3{}^0} + \gamma\,(C_3 - C_3{}^0) \\ &+ \frac{1}{\lambda}\sum_{m=1}^{\infty} \frac{\theta^m}{m}\left\{\left(\frac{1}{\gamma C_3 + \theta}\right)^m - \left(\frac{1}{\gamma C_3{}^0 + \theta}\right)^m\right\} \sum_{n=1}^{\infty} \frac{1}{(m + n + 1)!}\,\frac{1}{(\lambda\theta)^{m+n}} \end{aligned} \tag{28}$$

Even though Equation (28) is a general solution for Z, it is inconvenient for practical use. Simpler expressions for Z will be derived later in this paper for some cases of practical interest.

The permeating velocity of solvent water (v_w) through the membrane can be expressed as

$$v_w = -\frac{1}{S}\frac{dV_1}{dt} \tag{29}$$

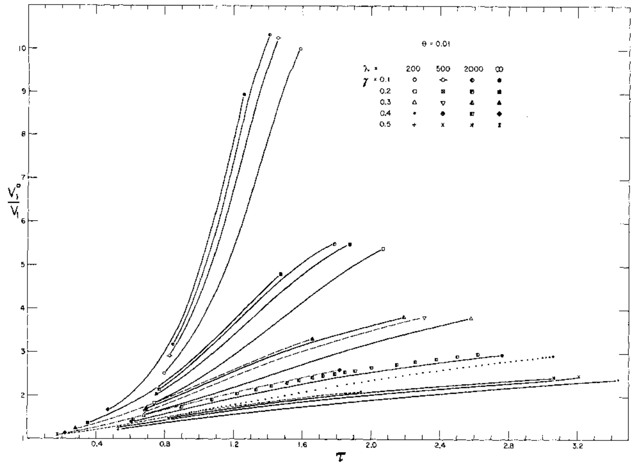

Fig. 1. τ vs. (V_1^0/V_1) for $\theta = 0.01$, $\gamma = 0.1$ to 0.5, and $\lambda = 200$ to ∞.

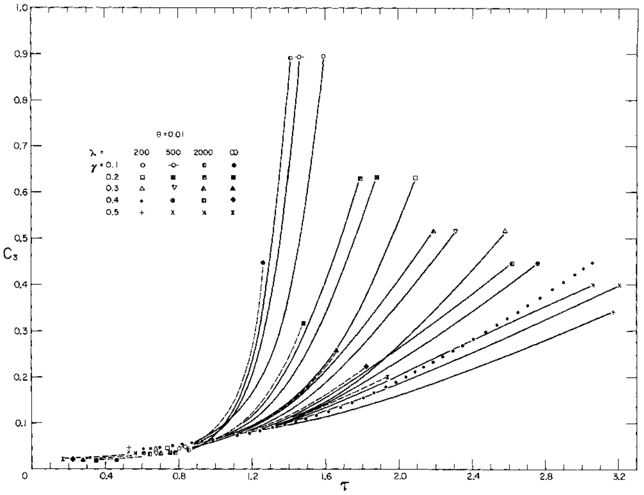

Fig. 3. τ vs. C_3 for $\theta = 0.01$, $\gamma = 0.1$ to 0.5, and $\lambda = 200$ to ∞.

where S is the area of the membrane surface. Combining Equations (13) and (29),

$$-\frac{1}{S}\frac{dV_1}{dt} = v_w^* \left[1 - \gamma(C_2 - C_3)\right] \quad (30)$$

From Equations (24) and (25),

$$V_1 = V_1^0 \exp(-Z) \quad (31)$$

$$\therefore dV_1 = -V_1^0 \exp(-Z)\, dZ \quad (32)$$

Combining Equations (30) and (32)

$$\frac{Sv_w^*}{V_1^0} dt = \frac{\exp(-Z)\, dZ}{1 - \gamma(C_2 - C_3)} \quad (33)$$

Let a dimensionless parameter τ, representing time, be defined as

$$\tau = \frac{S\, v_w^*\, t}{V_1^0} \quad (34)$$

From Equation (33),

$$\tau = \int_{C_3^0}^{C_3} \frac{\exp(-Z)\, \dfrac{dZ}{dC_3}}{1 - \gamma(C_2 - C_3)} dC_3 \quad (35)$$

From Equation (16),

$$C_2 - C_3 = \frac{C_3}{(\gamma C_3 + \theta)} \quad (36)$$

and

$$1 - \gamma(C_2 - C_3) = \frac{\theta}{(\gamma C_3 + \theta)} \quad (37)$$

Substituting for dZ/dC_3 from Equation (27),

$$\tau = \int_{C_3^0}^{C_3} \left[\frac{\gamma}{\lambda(\gamma C_3 + \theta)} - \gamma + \frac{(\gamma C_3 + \theta)}{C_3} \right\} (\gamma C_3 + \theta)$$

$$\exp \frac{1}{\lambda(\gamma C_3 + \theta)} + 1 \left. \right\} \Bigg] \frac{\exp(-Z)}{\theta} dC_3 \quad (38)$$

It does not seem possible to obtain an analytical solution to Equation (38), but τ may be evaluated by numerical integration as functions of γ, θ, and λ for any assumed value of C_3. For this integration, C_3^0 is obtained from the simultaneous solutions of the following equations obtained from Equations (16) and (17) which, at $t = 0$, become

$$C_2^0 = \left[1 + \frac{1}{(\gamma C_3^0 + \theta)}\right] C_3^0 \quad (39)$$

and

$$C_3^0 = \frac{\sqrt{(1 + \theta - \gamma C_2^0)^2 + 4\gamma\theta C_2^0} - (1 + \theta - \gamma C_2^0)}{2\gamma} \quad (40)$$

The instantaneous solute separation f may be defined as

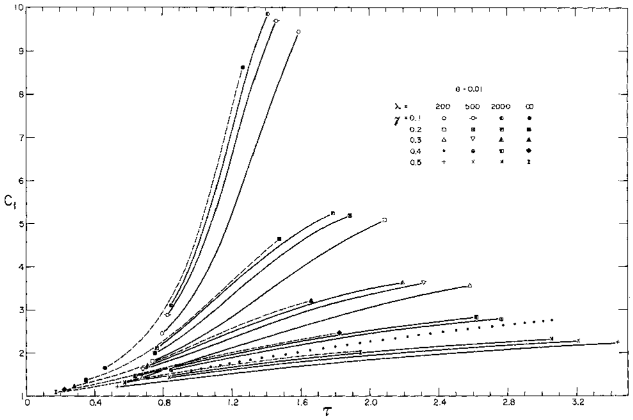

Fig. 2. τ vs. C_1 for $\theta = 0.01$, $\gamma = 0.1$ to 0.5, and $\lambda = 200$ to ∞.

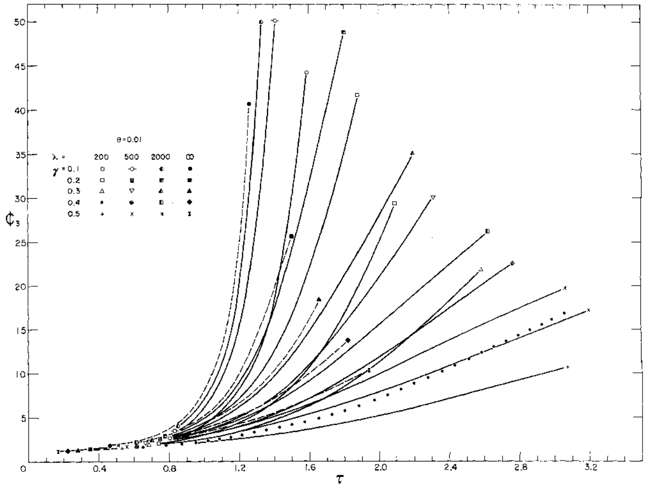

Fig. 4. τ vs. $\cancel{C}_3$ for $\theta = 0.01$, $\gamma = 0.1$ to 0.5, and $\lambda = 200$ to ∞.

$$f = 1 - \frac{C_3}{C_1} \tag{41}$$

Using Equation (14) again,

$$f = 1 - \frac{1}{q} \tag{42}$$

or

$$f = \frac{\exp\left[-\dfrac{1}{\lambda(\gamma C_3 + \theta)}\right]}{(\gamma C_3 + \theta) + \exp\left[-\dfrac{1}{\lambda(\gamma C_3 + \theta)}\right]} \tag{43}$$

Also, from Equations (13), and (36),

$$(v_w/v_w^*) = \frac{\theta}{(\gamma C_3 + \theta)} \tag{44}$$

$$(v_w/v_w^0) = \frac{1 - \gamma(C_2 - C_3)}{1 - \gamma(C_2^0 - C_3^0)} \tag{45}$$

Thus for the general case of the batch-by-batch process, the dimensionless quantities (V_1/V_1^0), Z, τ, C_1, C_2, C_2^0, C_3^0, q, f, (v_w/v_w^*), and (v_w/v_w^0) are expressed by Equations (24), (28), (38), (14), (16), (39), (40), (15), (43), (44), and (45) respectively, and their magnitudes can be calculated for any assumed value of C_3 with reference to any particular system specified by the parameters γ, θ, and λ. The correlations of (V_1/V_1^0), C_1, C_3, $\not{C}_3$, q, and (v_w/v_w^0) as functions of τ are particularly convenient for reverse osmosis process design. A set of such correlations is illustrated in Figures 1 to 6. An extensive compilation of such correlations may prove very useful for design purposes.

The points in the Figures 1 to 12 are not experimental data; they simply identify the lines, the data for which were obtained by computer calculations.

SOME SPECIAL CASES OF THE BATCH-BY-BATCH PROCESS

Case 1: $\gamma = 0$, and $\lambda \rightarrow \infty$

This limiting case is of interest both for purposes of comparison with actual cases, and as an approximation to those practical cases where the osmotic pressure and concentration polarization effects are negligible. Using Equations (13), (14), (15), (24), (33), and (42) for the special case, the following relationships are obtained.

$$(v_w/v_w^*) = 1 \tag{46}$$

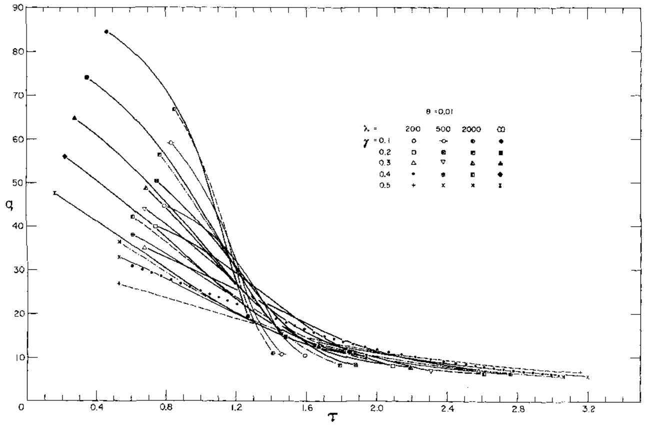

Fig. 5. τ vs. q for $\theta = 0.01$, $\gamma = 0.1$ to 0.5, and $\lambda = 200$ to ∞.

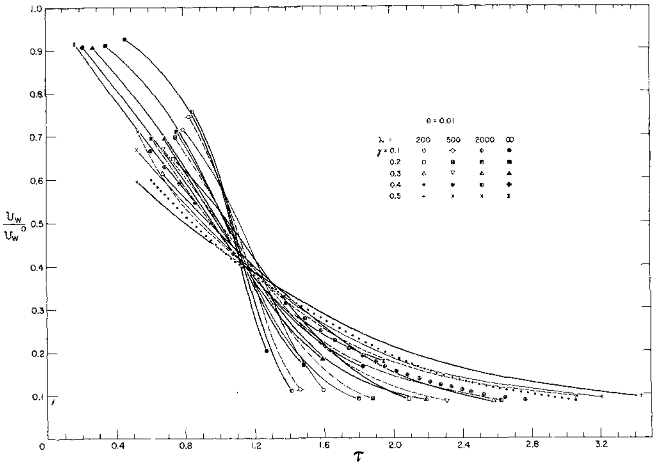

Fig. 6. τ vs. (v_w/v_w^0) for $\theta = 0.01$, $\gamma = 0.1$ to 0.5, and $\lambda = 200$ to ∞.

$$(v_w/v_w^0) = 1 \tag{47}$$

$$q = \frac{1+\theta}{\theta} \tag{48}$$

$$f = \frac{1}{1+\theta} \tag{49}$$

$$C_1 = C_3\left[\frac{1+\theta}{\theta}\right] \tag{50}$$

$$C_2 = C_1 \tag{51}$$

$$C_2^0 = C_1^0 = 1 \tag{52}$$

$$C_3 = \frac{C_1\,\theta}{1+\theta} \tag{53}$$

$$C_3^0 = \frac{C_1^0\,\theta}{1+\theta} = \frac{\theta}{1+\theta} \tag{54}$$

$$C_1 - C_3 = \frac{C_1}{1+\theta} \tag{55}$$

$$\ln\frac{V_1}{V_1^0} = -\int_1^{C_1} (1+\theta)\,\frac{dC_1}{C_1} \tag{56}$$

$$= -\,(1+\theta)\ln C_1 \tag{57}$$

$$\therefore Z = (1+\theta)\ln C_1 \tag{58}$$

$$dZ = (1+\theta)\,\frac{dC_1}{C_1} \tag{59}$$

$$\tau = \int \exp(-Z)\,dZ \tag{60}$$

$$= \int_1^{C_1} (1+\theta)\,C_1^{-(1+\theta)}\,\frac{dC_1}{C_1} \tag{61}$$

$$= 1 - C_1^{-(1+\theta)} \tag{62}$$

Thus for the special case $\gamma = 0$, and $\lambda \rightarrow \infty$, the quantities (V_1/V_1^0), Z, τ, C_1, C_2, C_2^0, C_3^0, q, f, (v_w/v_w^*) and (v_w/v_w^0) are expressed by Equations (57), (58), (62), (50), (51), (52), (54), (48), (49), (46), and (47) respectively, and their magnitudes can be calculated for any assumed value of C_3 with reference to any particular system specified by the parameter θ. Further, from Equation (62),

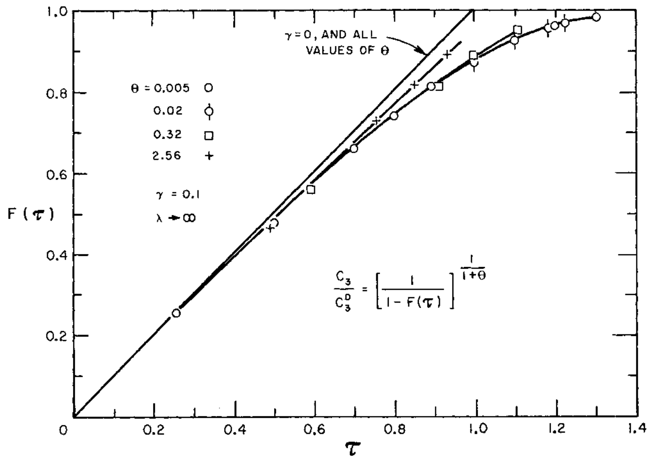

Fig. 7. τ **vs.** $F(\tau)$ **for** $\gamma = 0.1$, $\theta = 0.005$ **to 0.56 and** $\lambda = \infty$.

$$C_1 = \left[\frac{1}{1-\tau}\right]^{\frac{1}{(1+\theta)}} \tag{63}$$

Using Equations (53) and (54),

$$C_3 = C_3{}^0\left[\frac{1}{1-\tau}\right]^{\frac{1}{1+\theta}} \tag{64}$$

$$\therefore\ C_3 = \frac{C_3}{C_3{}^0} = \left[\frac{1}{1-\tau}\right]^{\frac{1}{(1+\theta)}} \tag{65}$$

The form of Equation (65) is particularly interesting for practical design purposes, and its use will be discussed in the next section.

Case 2: $\lambda \to \infty$

This limiting case is of interest both for purposes of comparison with actual cases, and also as an approximation to practical cases involving extremely high mass transfer coefficients, or very efficient stirring in the vicinity of the membrane surface on the high pressure side. Using Equations (13), (14), (15), (16), (17), and (27) for the above special case, the following equations are obtained.

$$q = 1 + \frac{1}{(\gamma C_3 + \theta)} \tag{66}$$

$$f = 1 - \frac{1}{q} = \frac{1}{(\gamma C_3 + \theta + 1)} \tag{67}$$

$$C_2 = C_1 \tag{51}$$

$$C_2{}^0 = C_1{}^0 = 1 \tag{52}$$

$$C_1 = \left[1 + \frac{1}{(\gamma C_3 + \theta)}\right] C_3 \tag{68}$$

$$C_3 = \frac{\sqrt{(1+\theta-\gamma C_1)^2 + 4\gamma\theta C_1} - (1+\theta-\gamma C_1)}{2\gamma} \tag{69}$$

$$C_3{}^0 = \frac{\sqrt{(1+\theta-\gamma)^2 + 4\gamma\theta} - (1+\theta-\gamma)}{2\gamma} \tag{70}$$

$$(v_w/v_w{}^*) = 1 - \gamma(C_1 - C_3) \tag{71}$$

$$(v_w/v_w{}^0) = \frac{1-\gamma(C_1-C_3)}{1-\gamma(1-C_3{}^0)} \tag{72}$$

$$Z = \gamma(C_3 - C_3{}^0) + (1+\theta)\ln\frac{C_3}{C_3{}^0} - \ln\left[\frac{C_3 + \dfrac{\theta}{\gamma}}{C_3{}^0 + \dfrac{\theta}{\gamma}}\right] \tag{73}$$

$$\therefore\ \ln\frac{V_1}{V_1{}^0} = - \left[\gamma(C_3 - C_3{}^0) + (1+\theta)\ln\frac{C_3}{C_3{}^0} - \ln\frac{\left(C_3 + \dfrac{\theta}{\gamma}\right)}{\left(C_3{}^0 + \dfrac{\theta}{\gamma}\right)}\right] \tag{74}$$

From Equations (33) and (37)

$$\frac{S\, v_w{}^*\, dt}{V_1{}^0} = \frac{\exp(-Z)\,dZ}{1-\gamma(C_1-C_3)} \tag{75}$$

and

$$1 - \gamma(C_1 - C_3) = \frac{\theta}{(\gamma C_3 + \theta)} \tag{76}$$

Differentiating Equation (73), and substituting in Equation (75),

$$\tau = \int_{C_3{}^0}^{C_3}\left[\frac{(\gamma C_3 + \theta)^2}{C_3\theta} + \frac{1}{C_3}\right]\exp(-Z)\,dC_3 \tag{77}$$

where

$$\exp(-Z) = \left[\frac{C_3}{C_3{}^0}\right]^{-(1+\theta)} \left[\frac{C_3 + \dfrac{\theta}{\gamma}}{C_3{}^0 + \dfrac{\theta}{\gamma}}\right] \exp[-\gamma(C_3 - C_3{}^0)] \tag{78}$$

Thus for the special case $\lambda \to \infty$, the quantities $(V_1/V_1{}^0)$, Z, τ, C_1, C_2, $C_2{}^0$, $C_3{}^0$, q, f, $(v_w/v_w{}^*)$, and $(v_w/v^0{}_w)$ are expressed by Equations (74), (73), (77), (68), (50), (51), (70), (66), (67), (71), and (72) respectively, and their magnitudes can be calculated for any assumed value of C_3 with reference to any particular system specified by the parameters γ and θ.

Further, following the form of Equation (65), one may express

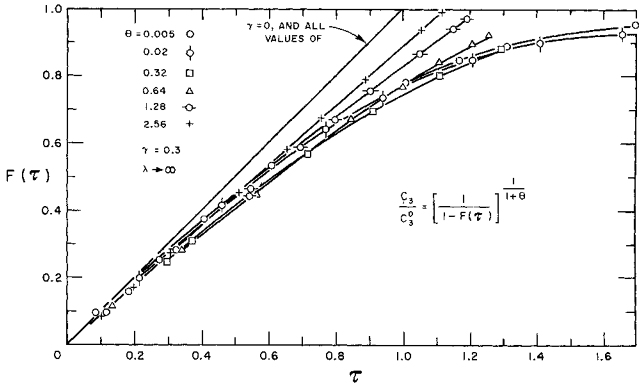

Fig. 8. τ **vs.** $F(\tau)$ **for** $\gamma = 0.3$, $\theta = 0.005$ **to 2.56 and** $\lambda = \infty$.

$$C_3 = \frac{C_3}{C_3^0} = \left[\frac{1}{1-F(\tau)}\right]^{\frac{1}{1+\theta}} \tag{79}$$

and establish a correlation between τ and $F(\tau)$ for different values of γ and θ for the case $\lambda \to \infty$. A set of such correlations is illustrated in Figures 7, 8, and 9. Such correlations are extremely useful for a quick evaluation of C_3 for any given value of τ.

Case 3: λ is large and finite, and $\lambda\theta > 1$

In most cases of practical interest, the mass transfer coefficient is sufficiently large so that λ becomes large and $\lambda\theta$ is greater than 1. When λ is large,

$$\exp\left[-\frac{1}{\lambda(\gamma C_3+\theta)}\right] \approx 1 - \frac{1}{\lambda(\gamma C_3+\theta)} \tag{80}$$

$$\therefore q = 1 + \frac{1}{(\gamma C_3+\theta)}\left[1 - \frac{1}{\lambda(\gamma C_3+\theta)}\right] \tag{81}$$

$$= 1 + \frac{1}{(\gamma C_3+\theta)} - \frac{1}{\lambda(\gamma C_3+\theta)^2} \tag{82}$$

or

$$q - 1 = \frac{\lambda(\gamma C_3+\theta)-1}{\lambda(\gamma C_3+\theta)^2} \tag{83}$$

$$\therefore f = 1 - \frac{1}{q} = \frac{q-1}{q} \tag{42}$$

$$= \left[\frac{\lambda(\gamma C_3+\theta)-1}{\lambda(\gamma C_3+\theta)^2}\right] \Big/ \left[1 + \frac{1}{(\gamma C_3+\theta)} - \frac{1}{\lambda(\gamma C_3+\theta)^2}\right] \tag{84}$$

$$C_1 = C_3\, q \tag{14}$$

$$= \left[1 + \frac{1}{(\gamma C_3+\theta)} - \frac{1}{\lambda(\gamma C_3+\theta)^2}\right] C_3 \tag{85}$$

Differentiating Equation (85), and evaluating $C_3\,(q-1)$,

$$dC_1 = \left[1 + \frac{\theta}{(\gamma C_3+\theta)^2} - \frac{\theta-\gamma C_3}{\lambda(\gamma C_3+\theta)^3}\right] dC_3 \tag{86}$$

$$\frac{1}{C_3(q-1)} = \frac{\lambda(\gamma C_3+\theta)^2}{C_3[\lambda(\gamma C_3+\theta)-1]} \tag{87}$$

$$Z = \int_{C_3^0}^{C_3} \frac{dC_1}{C_3(q-1)} \tag{25}$$

$$= \int_{C_3^0}^{C_3} \left[\frac{\lambda(\gamma C_3+\theta)^2}{C_3[\lambda(\gamma C_3+\theta)-1]} + \frac{\lambda\theta+1}{C_3[\lambda(\gamma C_3+\theta)-1]} - \frac{2\theta}{C_3(\gamma C_3+\theta)[\lambda(\gamma C_3+\theta)-1]}\right] dC_3 \tag{88}$$

$$= \gamma(C_3 - C_3^0) + \left[1 + \theta + \frac{\theta}{(\lambda\theta-1)}\right] \ln\frac{C_3}{C_3^0} - 2\ln\left(\frac{C_3+\frac{\theta}{\gamma}}{C_3^0+\frac{\theta}{\gamma}}\right) + \left[1 - \frac{1}{\lambda(\lambda\theta-1)}\right] \ln\left(\frac{C_3+\frac{\theta}{\gamma}-\frac{1}{\gamma\lambda}}{C_3^0+\frac{\theta}{\gamma}-\frac{1}{\gamma\lambda}}\right) \tag{89}$$

$$\therefore \ln\frac{V_1}{V_1^0} = -\gamma(C_3 - C_3^0) - \left[1 + \theta + \frac{\theta}{(\lambda\theta+1)}\right] \ln\frac{C_3}{C_3^0} + 2\ln\left(\frac{C_3+\frac{\theta}{\gamma}}{C_3^0+\frac{\theta}{\gamma}}\right) - \left[1 - \frac{1}{\lambda(\lambda\theta-1)}\right] \ln\left(\frac{C_3+\frac{\theta}{\gamma}-\frac{1}{\gamma\lambda}}{C_3^0+\frac{\theta}{\gamma}-\frac{1}{\gamma\lambda}}\right) \tag{90}$$

Differentiating Equation (89),

$$\frac{dZ}{dC_3} = \gamma - \frac{2}{C_3+\frac{\theta}{\gamma}} + \left[1 + \theta + \frac{\theta}{(\lambda\theta-1)}\right]\frac{1}{C_3} + \left[1 - \frac{1}{\lambda(\lambda\theta-1)}\right] \frac{1}{\left(C_3+\frac{\theta}{\gamma}-\frac{1}{\gamma\lambda}\right)} \tag{91}$$

Let

$$\frac{dZ}{dC_3} = F_1(C_3) \tag{92}$$

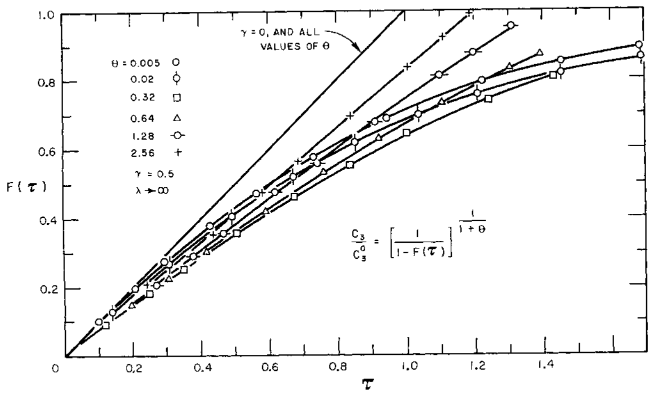

Fig. 9. τ vs. $F(\tau)$ for $\gamma = 0.5$, $\theta = 0.005$ to 2.56 and $\lambda = \infty$.

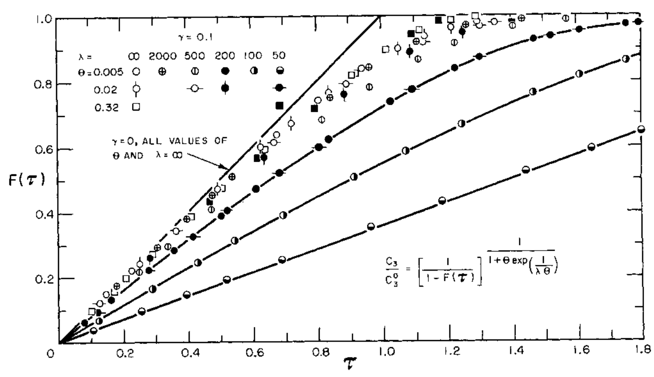

Fig. 10. τ vs. $F(\tau)$ for $\gamma = 0.1$, $\theta = 0.005$ to 0.32, and $\lambda = 50$ to ∞.

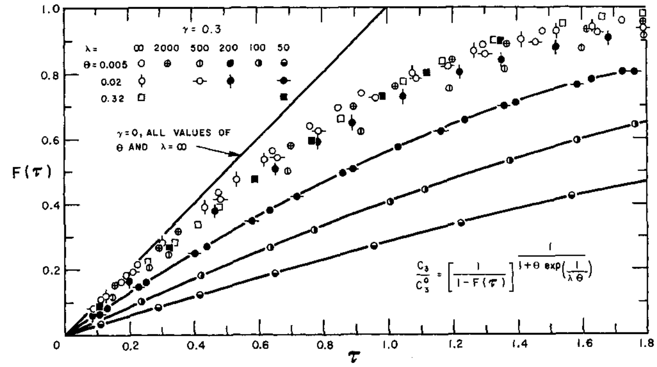

Fig. 11. τ vs. $F(\tau)$ for $\gamma = 0.3$, $\theta = 0.005$ to 0.32, and $\lambda = 50$ to ∞.

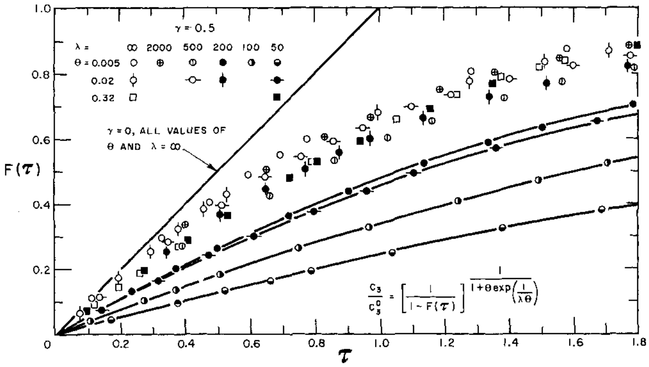

Fig. 12. τ vs. $F(\tau)$ for $\gamma = 0.5$, $\theta = 0.005$ to 0.32, and $\lambda = 50$ to ∞.

$$\tau = \int_{c_3^0}^{c_3} \frac{\exp(-Z)\,\dfrac{dZ}{dC_3}}{1-\gamma(C_2-C_3)}\,dC_3 \tag{35}$$

Using Equations (36) and (92),

$$\tau = \int_{c_3^0}^{c_3} \frac{(\gamma C_3+\theta)}{\theta}\,F_1(C_3)\exp(-Z)\,dC_3 \tag{93}$$

Thus for the case λ is large and $\lambda\theta > 1$, (V_1/V_1^0), Z, τ, C_1, q, and f are expressed by Equations (90), (89), (93), (85), (82), and (84) respectively; and C_2, C_2^0, C_3^0, (v_w/v_w^*), and (v_w/v_w^0) are expressed by Equations (16), (39), (40), (44), and (45) respectively as in the general case.

Further following the form of Equations (65) and (79), one may express

$$C_3 = \frac{C_3}{C_3^0} = \left[\frac{1}{1-F(\tau)}\right]^{\frac{1}{1+\theta\exp\frac{1}{\lambda\theta}}} \tag{94}$$

and establish a correlation between τ and $F(\tau)$ for different values of γ, θ, and λ. A set of such correlations is illustrated in Figures 10, 11, and 12 which show that the values of $F(\tau)$ are essentially the same for a given value of $\lambda\theta$. The latter observation suggests that the quantity $\lambda\theta$ is a particularly useful design parameter.

Case 4: $\gamma = 0$

This case is an approximation to practical cases where the osmotic pressure of the solution is negligible. From Equations (15), (27), and (35), q, Z, and C_3 for the above case may be expressed as

$$q = 1 + \frac{1}{\theta}\exp\left(-\frac{1}{\lambda\theta}\right) \tag{95}$$

$$Z = \left[1+\theta\exp\left(\frac{1}{\lambda\theta}\right)\right]\ln C_3 \tag{96}$$

and

$$C_3 = \left[\frac{1}{1-\tau}\right]^{\frac{1}{1+\theta\exp\left(\frac{1}{\lambda\theta}\right)}} \tag{97}$$

EQUATIONS FOR THE FLOW PROCESS

Consider the reverse osmosis process for feed flow through a channel. The geometry of the channel is immaterial for this discussion. Let $1/h$ be defined as membrane area per unit volume of channel space. Let $\bar{u}^0$ and $\bar{u}$ be the average velocity of feed at channel entrance, and at a longitudinal distance x from channel entrance respectively. From the water and solute material balance over a differential length dx at distance x from channel entrance (Figure 13) the following equations are obtained.

$$\bar{u} = \bar{u} + \frac{d\bar{u}}{dx}dx + \left(\frac{v_w}{h}\right)dx \tag{98}$$

$$\therefore -\frac{d\bar{u}}{dx} = \frac{v_w}{h} \tag{99}$$

$$\bar{u}C_1 = \bar{u}C_1 + \frac{d}{dx}(\bar{u}C_1)\,dx + C_3\left(\frac{v_w}{h}\right)dx \tag{100}$$

$$\therefore -\frac{d}{dx}(\bar{u}C_1) = \frac{C_3 v_w}{h} \tag{101}$$

$$= -C_3\frac{d\bar{u}}{dx} \tag{102}$$

$$\bar{u}\frac{dC_1}{dx} + C_1\frac{d\bar{u}}{dx} = C_3\frac{d\bar{u}}{dx} \tag{103}$$

$$\bar{u}\frac{dC_1}{dx} = -(C_1-C_3)\frac{d\bar{u}}{dx} \tag{104}$$

$$\frac{d\bar{u}}{\bar{u}} = -\frac{dC_1}{C_1-C_3} \tag{105}$$

The right side of Equation (105) is identical to that of Equation (23) given for the batch-by-batch operation. Comparing the dimensionless parameters

$$X = \frac{v_w^*}{\bar{u}^0}\frac{x}{h} \tag{106}$$

and

$$\tau = \frac{S\,v_w^*\,t}{V_1^0} \tag{34}$$

it is evident that at time $t = 0$, $1/h$ in Equation (106) is the same as membrane area per unit initial volume of feed solution, S/V_1^0, in Equation (34), and distance x from channel entrance divided by velocity at channel entrance, $x/\bar{u}^0$, in Equation (106) is the same as time elapsed from the start of the operation, t, in Equation (34). Consequently when S/V_1^0 and t in the batch-by-

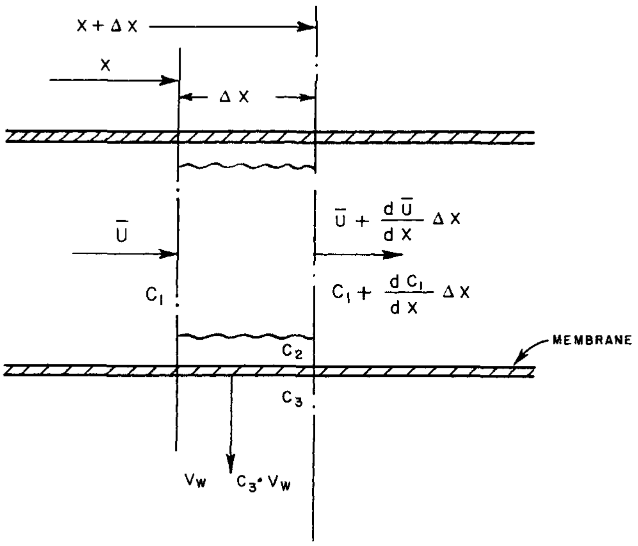

Fig. 13. Schematic diagram for the reverse osmosis flow process.

batch operation are replaced by $1/h$ and $(x/\bar{u}^0)$ respectively for the flow process, τ for the batch process corresponds identically to X for the flow process; and, on the basis of Equation (105), all the correlations developed above for the batch process when expressed as functions of τ become applicable for the flow process when expressed as functions of X.

CONCLUSIONS

The dimensionless quantities γ, θ, and λ are the basic design parameters for the reverse osmosis membrane separation process. When any solution-membrane-operating system is specified by the above parameters, the general equations presented in this paper offer a means of predicting membrane performance for different operating conditions, and establishing the optimum conditions of operation for a given performance. Thus the reverse osmosis membrane separation process can be treated as a general unit operation in chemical engineering.

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NOTATION

A = pure water permeability constant, g.mole H_2O/sq. cm. sec. atm.
B = proportionality constant defined by Equation (4), atm.
B' = proportionality constant defined by Equation (4), atm. cc./g. mole
c = molar density of solution, g. mole/cc.
c_A = molar concentration of solute, g. mole/cc.
C = c_A/c_{A1}^0
C_3 = c_{A3}/c_{A3}^0
D_{AM} = diffusivity of solute through the membrane, sq. cm./sec.
$(D_{AM}/K\delta)$ = solute transport parameter for membrane, cm./sec.
f = solute separation defined by Equation (41)
$(1/h)$ = area of membrane surface per unit volume of channel space, cm.$^{-1}$
k = mass transfer coefficient on the high pressure side of the membrane, cm./sec.
N_B = solvent water flux through the membrane, g. mole/sq. cm./sec.
P = operating pressure, atm.
q = quantity defined by Equation (14)
S = area of membrane surface, sq. cm.
t = time, sec.
$\bar{u}$ = average fluid velocity in the transverse length of the channel at a given x, cm./sec.
v_w = fluid velocity component in the direction perpendicular to the membrane surface, cm./sec.
v_w^* = quantity defined by Equation (6), cm./sec.
V = volume of solution on the high pressure side of the membrane, cc.
x = longitudinal distance from channel entrance, cm.
X = quantity defined by Equation (103)
X_A = mole fraction of solute
Z = quantity defined by Equation (25)

Greek Letters

γ = quantity defined by Equation (1)
γ^* = quantity defined by Equation (5), cc./g. mole
δ = effective thickness of membrane, cm.
θ = quantity defined by Equation (2)
λ = quantity defined by Equation (3)
$\pi(X_A)$ = osmotic pressure corresponding to X_A, atm.
τ = quantity defined by Equation (34)

Subscripts

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

Superscript

0 = initial condition for the batch process, or condition at channel entrance for the flow process

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