

A Review of Reverse Osmosis Theory

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Many mechanistic and mathematical models have been proposed to describe reverse osmosis membranes. Some of these descriptions rely on relatively simple concepts while others are far more complex and require sophisticated solution techniques. Models that adequately describe the performance of RO membranes are very important since these are needed in the design of RO processes. Models that predict separation characteristics also minimize the number of experiments that must be performed to describe a particular system. Excellent reviews of membrane transport models and mechanisms include Jonsson (1980), Soltanieh and Gill (1981), Mazid (1984), Pusch (1986), Dickson (1988), Rautenbach and Albrecht (1989), and Bhattacharyya and Williams (1992c).

Reverse osmosis models can be divided into three types: irreversible thermodynamics models (such as Kedem-Katchalsky and Spiegler-Kedem models); nonporous or homogeneous membrane models (such as the solution-diffusion, solution-diffusion-imperfection, and extended solution-diffusion models); and pore models (such as the finely-porous, preferential sorption-capillary flow, and surface force-pore flow models). Charged RO membranes theories can be used to describe nanofiltration membranes, which are often negatively charged; these models (such as Donnan exclusion and extended Nernst-Planck models) include electrostatic effects. The transport models focus on the top thin skin of asymmetric membranes or the top thin skin layer of composite membranes since these determine fluxes and selectivities of most membranes (Bhattacharyya and Williams, 1992c). Also, most of the membrane models assume equilibrium (or near equilibrium) or steady state conditions in the membrane.

A fundamental difference exists between the assumptions of the homogeneous and porous membrane models. The homogeneous models assume that the membrane is nonporous; that is, transport takes place between the interstitial spaces of the polymer chains or polymer nodules, usually by diffusion. The porous models assume that transport takes place through pores that run the length of the membrane barrier layer; as a result, transport can occur by both diffusion and convection through the pores. While both conceptual models have had some success in predicting RO separations, the question of whether a RO membrane is truly homogeneous (no pores) or porous is still a point of debate. No technique is currently available to definitively answer this question.

Some of the most important RO membrane transport theories and models are reviewed below. Concentration polarization, the effects of RO process variables on membrane performance, and water-solute-membrane interactions are also discussed.

Irreversible Thermodynamics Models

Some of the earliest RO membrane models were based on the principles of irreversible thermodynamics; Soltanieh and Gill (1981) and Baranowski (1991) provide excellent discussions of the development and applicability of these models. Irreversible thermodynamics models assume the membrane is not far from equilibrium and so fluxes can be described by phenomenological relationships (Jonsson, 1980; Soltanieh and Gill, 1981; Dickson, 1988; van den Berg and Smolders, 1992). One of the early models was that derived by Kedem and Katchalsky (Kedem and Katchalsky, 1958; Jonsson, 1980; Soltanieh and Gill, 1981; Dickson, 1988; Bhattacharyya and Williams, 1992c):

$$J_w = L_p (\Delta P - \sigma \Delta \pi) \quad \text{Eqn. 1}$$

$$J_s = \omega \Delta \pi + (1 - \sigma) (C_m)_{avg} J_w \quad \text{Eqn. 2}$$

where L_p , ω , and σ , defined as the Staverman reflection coefficient $\sigma \equiv \left(\frac{\Delta P}{\Delta \pi} \right)_{J_w=0}$, are functions of the phenomenological coefficients and $(C_m)_{avg}$ is the logarithmic mean solute concentration in the membrane¹. The reflection coefficient represents coupling of solute and solvent flux through the membrane. Pusch (1977) derived an expression for solute rejection as

$$\frac{I}{R} = \frac{I}{\sigma} + \left(\frac{L_\pi}{L_p} - \sigma^2 \right) \left(\frac{L_p}{\sigma} \right) \pi_F \frac{I}{J_w} \quad \text{Eqn. 3}$$

where L_π is determined from $\omega = \left(\frac{L_\pi}{L_p} - \sigma^2 \right) (C_m)_{avg} L_p$. A disadvantage of the Kedem-Katchalsky model is that the coefficients in Equations 1, 2, and 3 can be functions of concentration (Jonsson, 1980; Soltanieh and Gill, 1981; Dickson, 1988).

To avoid concentration dependence of the transport parameters, Spiegler and Kedem (1966) defined local water (P_w) and solute (P_s) permeabilities and reflection coefficients and then represented the fluxes as

$$J_w = -P_w \left(\frac{dP}{dz} - \sigma \frac{d\pi}{dz} \right) \quad \text{Eqn. 4}$$

$$J_s = -P_s \frac{dC_m}{dz} + (1 - \sigma) C_m J_w \quad \text{Eqn. 5}$$

which can be integrated to (Spiegler and Kedem, 1966; Jonsson, 1980; Dickson, 1988)

$$\frac{I}{R} = \frac{1 - \sigma \exp \left(-(1 - \sigma) \frac{\delta J_w}{P_s} \right)}{\sigma \left[1 - \exp \left(-(1 - \sigma) \frac{\delta J_w}{P_s} \right) \right]}. \quad \text{Eqn. 6}$$

The Spiegler-Kedem model has found wide use for the description and analysis of RO membrane separations.

While irreversible thermodynamics can describe RO membrane transport, a major disadvantage of these models is the treatment of the membrane as a "black box" (Dickson, 1988); that is, these models provide no insight into the transport mechanisms of the membrane. As a result, irreversible thermodynamics models are not very useful for optimizing separations based on

¹ Note here and in the other models discussed it is assumed that the bulk feed solution concentration is equal to the membrane wall solution concentration; while this is not always true these can usually be related with the appropriate concentration polarization expressions such as those discussed later.

membrane structure and properties. These models also do not adequately describe water flux for some solute systems; in particular, some dilute organics (with $\pi_F = \pi_P = 0$) have substantially lower water fluxes than those described by Equation 1.

Diffusion-Based Models

Solution-Diffusion Model

The solution-diffusion (SD) model was proposed by Lonsdale et al. (1965); as its name implies, this model is based on diffusion of the solute and solvent through the membrane. The model assumes that (Lonsdale et al., 1965; Soltanieh and Gill, 1981; Bhattacharyya and Williams, 1992c): (1) the RO membrane has a homogeneous, nonporous surface layer; (2) both the solute and solvent dissolve in this layer and then each diffuses across it; (3) the solute and solvent diffusion is uncoupled and due to its own chemical potential gradient across the membrane; (4) these gradients are the result of concentration and pressure differences across the membrane. Differences in the solubilities (partition coefficients) and diffusivities of the solute and solvent in the membrane phase are extremely important in this model since these strongly influence fluxes through the membrane. The derivation of the SD model is given in Lonsdale et al. (1965) and Soltanieh and Gill (1981) and is summarized here.

A solution-diffusion type membrane is shown schematically in Figure 1. The water transport across the membrane is only by diffusion and so can be expressed by Fick's law as

$$J_w = - D_{wm} \frac{dC_{wm}}{dz} \quad \text{Eqn. 7}$$

where C_{wm} is the water concentration in the membrane and D_{wm} is the water diffusivity in the membrane. Assuming the water-membrane solution obeys Henry's law,

$$d\mu_w = - R_g T d(\ln C_{wm}) = - R_g T \frac{dC_{wm}}{C_{wm}} \quad \text{Eqn. 8}$$

and substituting Equation 8 in 7 results in

$$J_w = \frac{D_{wm} C_{wm}}{R_g T} \frac{d\mu_w}{dz} \approx \frac{D_{wm} C_{wm}}{R_g T} \frac{\Delta\mu_w}{\delta} \quad \text{Eqn. 9}$$

The membrane water chemical potential change is given by

$$\Delta\mu_w = R_g T \ln \Delta a_w + \bar{V}_w \Delta P \quad \text{Eqn. 10}$$

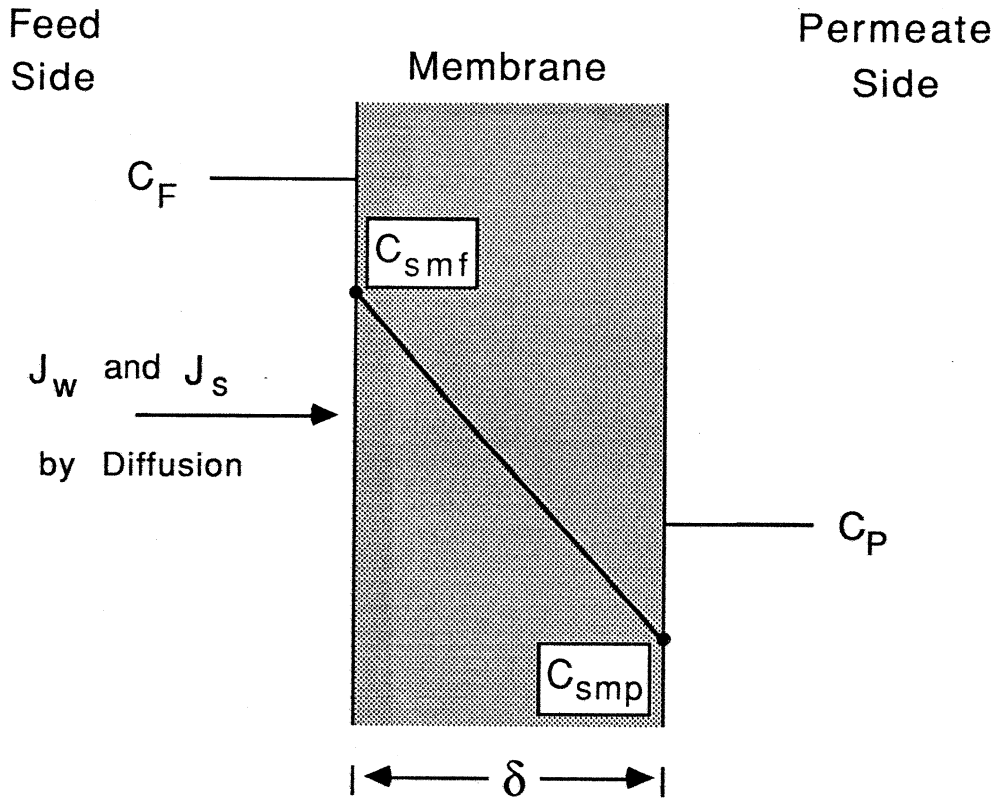


Figure 1. Schematic of a Solution-Diffusion Type Membrane.

where \bar{V}_w is the partial molar volume of water. Assuming \bar{V}_w does not vary significantly with pressure, the osmotic pressure is given by

$$\pi = \frac{-R_g T}{\bar{V}_w} \ln a_w \quad \text{Eqn. 11}$$

which, when substituted in Equation 10, results in

$$\Delta \mu_w = -\bar{V}_w \Delta \pi + \bar{V}_w \Delta P = \bar{V}_w (\Delta P - \Delta \pi). \quad \text{Eqn. 12}$$

Combining Equation 12 with Equation 9 gives an expression for water flux as

$$J_w = \frac{D_{wm} C_{wm} \bar{V}_w}{R_g T \delta} (\Delta P - \Delta \pi) \equiv A (\Delta P - \Delta \pi) \quad \text{Eqn. 13}$$

where A is termed the water permeability coefficient.

For the solute flux it is assumed that chemical potential difference due to pressure is negligible and so the driving force is almost entirely due to concentration differences. From Fick's law, the solute flux is

$$J_s = -D_{sm} \frac{dC_m}{dz} \approx D_{sm} \frac{\Delta C_m}{\delta} \quad \text{Eqn. 14}$$

where ΔC_m is the solute concentration difference across the membrane and D_{sm} is the solute diffusion coefficient in the membrane. The solute membrane concentration is related to the feed and permeate concentration by a partition coefficient assumed to be independent of concentration:

$$K_{sm} = \frac{C_{smf}}{C_F} = \frac{C_{smp}}{C_P}. \quad \text{Eqn. 15}$$

Substituting in the expression for the partition coefficient, the solute expression becomes

$$J_s = \frac{D_{sm} K_{sm}}{\delta} (C_F - C_P) \equiv B (C_F - C_P) \quad \text{Eqn. 16}$$

where B is referred to as the solute permeability coefficient. Using the relations for solvent and solute flux, solute rejection for the solution-diffusion model can be expressed as

$$\frac{I}{R} = I + \left(\frac{B}{A} \right) \left(\frac{I}{\Delta P - \Delta \pi} \right). \quad \text{Eqn. 17}$$

Equation 17 shows that as $\Delta P \rightarrow \infty$, $R \rightarrow I$. Comparison of the SD model Equations 13 and 16 with Equations 1 and 2 of the Kedem-Katchalsky model shows that these are equivalent for a membrane with perfect solute rejection ($\sigma = I$).

The principle advantage of the SD model is that only two parameters are needed to characterize the membrane system. As a result, it has been widely applied to both inorganic salt and organic solute systems. However, Soltanieh and Gill (1981) indicated that the SD model is limited to membranes with low water content; they and Mazid (1984) also have pointed out that for many RO membranes and solutes, particularly organics, the SD model does not adequately describe water or solute flux. They discuss possible causes for these deviations as suggested by other researchers, including imperfections in the membrane barrier layer, pore flow (convection effects), and solute-solvent-membrane interactions.

Solution-Diffusion-Imperfection Model

The solution-diffusion-imperfection model was an early modification of the solution-diffusion model to include pore flow in addition to diffusion of solvent and solute through a membrane as the mechanisms of transport (Sherwood et al., 1967). This model recognizes that there may be small imperfections or defects (pores) on the surface of membranes through which transport can occur.

Total water flux through the membrane is expressed as (Sherwood et al., 1967; Soltanieh and Gill, 1981; Bhattacharyya and Williams, 1992c):

$$N_w = K_1 (\Delta P - \Delta \pi) + K_2 \Delta P = J_w + K_2 \Delta P \quad \text{Eqn. 18}$$

where K_2 is a coupling coefficient describing pore flow. The first term in Equation 18 accounts for diffusive flux (K_1 is equivalent to a water permeability coefficient) while the second term is the pore flow contribution to the water flux. The total solute flux is given by

$$N_s = K_3 (C_F - C_P) + K_2 \Delta P = J_s + K_2 \Delta P. \quad \text{Eqn. 19}$$

The parameter K_3 is a solute permeability coefficient while the second term in Equation 19 accounts for solute pore flow through the membrane. Rejection for this model can be expressed as

$$\frac{I}{R} = I + \left(\frac{K_3}{K_1} \right) \left(\frac{I}{\Delta P - \Delta \pi} \right) + \left(\frac{K_2}{K_1} \right) \left(\frac{\Delta P}{\Delta P - \Delta \pi} \right). \quad \text{Eqn. 20}$$

While some researchers have shown that excellent fits of experimental data with the solution-diffusion-imperfection model are possible, the model has two major disadvantages: it contains three parameters that must be determined by nonlinear regression in order to characterize the membrane system; and the parameters describing the system are usually functions of both feed concentration and pressure (Soltanieh and Gill, 1981). Also, some dilute organic systems ($\Delta \pi = 0$) have substantially lower water fluxes than those predicted by Equation 18.

Extended Solution-Diffusion Model

Burghoff et al. (1980) recognized that the SD model does not explain the negative solute rejections found for some organics and so formulated the extended-solution-diffusion model. They pointed out that the SD model does not take into account possible pressure dependence of the solute chemical potential which, while negligible for inorganic salt solutions, can be important for organic solutes (Burghoff et al., 1980; Pusch, 1986; Dickson, 1988). Including the pressure dependent term, the chemical potential is given by

$$\Delta \mu_s = R_g T \ln \left(\frac{C_F}{C_P} \right) + \bar{V}_s \Delta P. \quad \text{Eqn. 21}$$

Using Equation 21, the solute flux can be written as

$$J_s = \frac{D_{sm} K_{sm}}{\delta} (C_F - C_P) + L_{sp} \Delta P \quad \text{Eqn. 22}$$

where L_{sp} represents the parameter responsible for solute transport due to the pressure difference across the membrane. The rejection is given by

$$\frac{I}{R} \left[I - \frac{L_{sp}}{A C_F} \left(I - \frac{\Delta\pi}{\Delta P} \right) \right] = I + \frac{B}{A(\Delta P - \Delta\pi)}. \quad \text{Eqn. 23}$$

Comparing Equations 2, 19, and 22 it can be seen that these have the same general form; however, these were derived using fundamentally different principles.

Burghoff et al. (1980) found that the negative rejections of phenol by a cellulose acetate membrane were adequately described by the extended-solution-diffusion model. However, this model has not been widely used for modelling RO membranes. Also, it still does not address the substantial decreases in water flux found for some dilute organic systems.

Pore Models

Preferential Sorption-Capillary Flow Model

An early pore model was the preferential sorption-capillary flow (PSCF) model proposed by Sourirajan (1970); this model assumes that the mechanism of separation is determined by both surface phenomena and fluid transport through pores in the RO membrane. In contrast to the SD model, the membrane is assumed to be microporous (Sourirajan, 1970; Sourirajan and Matsuura, 1985). The model states that the membrane barrier layer has chemical properties such that it has a preferential sorption for the solvent or preferential repulsion for the solutes of the feed solution. As a result, a layer of almost pure solvent is preferentially sorbed on the surface and in the pores of the membrane. Solvent transport occurs as solvent from this layer is forced through the membrane capillary pores under pressure.

The water flux according to this model is given by

$$N_w = A \{ \Delta P - [\pi(X_F) - \pi(X_P)] \} \quad \text{Eqn. 24}$$

where A is the pure water permeability constant of the membrane and $\pi(X)$ represents the osmotic pressure of the feed or permeate side with solute mole fraction X . The solute flux is expressed as

$$N_s = \frac{D_{sp} K_D C_T}{\delta} (X_F - X_P) \quad \text{Eqn. 25}$$

where K_D is the distribution coefficient of the solute from the feed into the pore of the membrane and D_{sp} is the diffusivity of the solute in the membrane pore. Solute rejection is given by

$$\frac{I}{R} = I + \frac{D_{sp} K_D C_T}{\delta} \frac{I}{A \{ \Delta P - [\pi(X_F) - \pi(X_P)] \}}. \quad \text{Eqn. 26}$$

It should be noted that although the forms of Equations 13 and 24 and Equations 16 and 25 appear virtually identical, the conceptual meaning of the parameters is greatly different. Sourirajan and Matsuura (1985) have utilized these equations to analyze transport for a large number of solutes and membranes. However, as for the SD model, water flux drop caused by some dilute organics as well as rejection for some solutes are not described by these equations.

Finely-Porous Model

The finely-porous model was first proposed by Merten (1966) and later in a modified form by Jonsson and Boesen (1975). This model assumes that transport of water takes place by viscous flow through uniform membrane pores and that transport of solute occurs by both diffusion and convection in these pores. The derivation is summarized here.

For the finely-porous model, a balance of applied and frictional forces acting on solute in a membrane pore with length $\tau\delta$ and radius R_p (see Figure 2) results in (Merten, 1966; Jonsson and Boesen, 1975; Soltanieh and Gill, 1981; Sourirajan and Matsuura, 1985):

$$F_s = -(F_{sw} + F_{sm}) \quad \text{Eqn. 27}$$

where F_s is the driving force for solute transport due to its chemical potential gradient, defined as

$$F_s = -\frac{d\mu_s}{dz} = -\frac{d\mu_s}{dC_{pore}} \frac{dC_{pore}}{dz} = -\frac{R_g T}{C_{pore}} \frac{dC_{pore}}{dz}, \quad \text{Eqn. 28}$$

F_{sw} is the friction force between solute and water,

$$F_{sw} = -X_{sw}(u_s - u); \quad \text{Eqn. 29}$$

and F_{sm} is the friction force between solute and the membrane pore,

$$F_{sm} = -X_{sm}(u_s - u_m) = -X_{sm}u_s = -X_{sm} \frac{J_s^{pore}}{C_{pore}} \quad \text{Eqn. 30}$$

where

$$u_s = \frac{J_s^{pore}}{C_{pore}}. \quad \text{Eqn. 31}$$

Using Equation 31, Equation 29 can be solved for the solute flux through a single pore as

$$J_s^{pore} = \frac{C_{pore}}{X_{sw}} (-F_{sw}) + u C_{pore}. \quad \text{Eqn. 32}$$

Combining Equations 28 and 30 with Equation 27 and rearranging results in

$$-F_{sw} = \frac{-R_g T}{C_{pore}} \frac{dC_{pore}}{dz} - X_{sm} \frac{J_s^{pore}}{C_{pore}} \quad \text{Eqn. 33}$$

and substituting Equation 33 in 32 and rearranging,

$$J_s^{pore} = \frac{-R_g T}{X_{sw} b} \frac{d C_{pore}}{dz} + \frac{u C_{pore}}{b} \quad \text{Eqn. 34}$$

where

$$b = \frac{X_{sw} + X_{sm}}{X_{sw}}. \quad \text{Eqn. 35}$$

Using

$$C_{pore}(\tau\delta) = \frac{J_s^{pore}}{u} \Big|_{z=\tau\delta} \quad \text{Eqn. 36}$$

with boundary conditions

$$C_{pore}(0) = K_D C_F \quad \text{Eqn. 37}$$

$$C_{pore}(\tau\delta) = K_D C_P \quad \text{Eqn. 38}$$

and assuming b , K_D , and X_{sw} are independent of solute concentration, Equation 34 can be integrated to

$$\frac{C_P}{C_F} = \frac{\exp\left(u\tau\delta \frac{X_{sw}}{R_g T}\right)}{1 + \frac{b}{K_D} \left[\exp\left(u\tau\delta \frac{X_{sw}}{R_g T}\right) - 1 \right]}. \quad \text{Eqn. 39}$$

The friction coefficient X_{sw} can be defined as

$$X_{sw} = \frac{R_g T}{D_{sw}}; \quad \text{Eqn. 40}$$

b is given by

$$b = \frac{D_{sw}}{D_{sm}}. \quad \text{Eqn. 41}$$

The parameter b is defined as the ratio of the frictional force acting on the solute moving in a membrane pore to the frictional force experienced by the solute in a free solution. It can be estimated using the Ferry-Faxen equation or a Ferry-Faxen-type equation; these equations were developed by considering the friction experienced by a molecule moving through a narrow pore. Equation 39 can be rewritten in terms of rejection as

$$R = 1 - \frac{\exp\left(u\tau\delta \frac{X_{sw}}{R_g T}\right)}{1 + \frac{b}{K_D} \left[\exp\left(u\tau\delta \frac{X_{sw}}{R_g T}\right) - 1 \right]}. \quad \text{Eqn. 42}$$

The viscous flow water flux through the membrane is determined by balancing the effective pressure driving force with the frictional force between the solute and pore wall; the water flux is given by (Jonsson and Boesen, 1975)

$$J_w = \varepsilon u = \frac{\varepsilon R_p^2 \Delta P}{8\eta\tau\delta} \left[\frac{1}{1 + \frac{R_p^2 X_{sm} C_P}{8\eta}} \right] \quad \text{Eqn. 43}$$

where ε is the porosity of the membrane and X_{sm} represents the frictional force between the solute and the membrane.

Jonsson and Boesen (1975) and Soltanieh and Gill (1981) pointed out that the finely-porous model can provide valuable insight into parameters such as pore size, solute-membrane interaction (friction parameter), and solute distribution coefficient that affect solute transport. Dickson (1988) indicated that the finely-porous model or modified finely-porous models (which contain different solute distribution coefficients on the feed and permeate side of the membrane) have been successfully used to predict solute separation. However, for some solute systems such as dilute organics, Equation 43 does not adequately describe decreases in water flux compared to the pure water flux unless a correction is made in the pore size; it is usually necessary to reduce the pore size in order for the measured and predicted water flux to agree. This disadvantage limits the finely-porous models applicability for water flux prediction for these systems.

Mehdizadeh (1990) pointed out an inconsistency in the original finely-porous model and developed a modified finely-porous model. The condition in Equation 36 is inconsistent with the concept of the finely-porous model in that it ignores the diffusive component of the flux at the pore outlet. The solute flux should be given by

$$J_s^{pore} \Big|_{z=\tau\delta} = \frac{-R_g T}{X_{sw} b} \frac{d C_{pore}}{dz} \Big|_{z=\tau\delta} + \frac{u C_{pore}}{b} \Big|_{z=\tau\delta}. \quad \text{Eqn. 44}$$

From a material balance on solute in the pore at steady state,

$$\frac{d J_s^{pore}}{dz} = 0 \quad \text{Eqn. 45}$$

and so Equation 34 can be rewritten as

$$\frac{d^2 C_{pore}}{dz} - \frac{u X_{sw}}{R_g T} \frac{d C_{pore}}{dz} = 0 \quad \text{Eqn. 46}$$

and integrated with Equations 37 and 38 as boundary conditions, giving the permeate concentration as

$$C_P = C_F - (C_F - C_P) \left[\frac{1 - \exp\left(u \frac{X_{sw}}{R_g T} z\right)}{1 - \exp\left(u \tau \delta \frac{X_{sw}}{R_g T}\right)} \right]. \quad \text{Eqn. 47}$$

Mehdizadeh solved Equation 47 for the permeate concentration by trial and error; however, Williams (1993) points out that this can be avoided with reformulation of the pore boundary conditions. Mehdizadeh compared his model with the original finely-porous model using the same parameters and found that the predicted permeate concentration of the modified finely-porous model was always higher than that of the original finely-porous model; this was expected since taking into account diffusive flux of the solute increases its predicted transport rate through the membrane pore. However, since both finely-porous models rely on measured separation data in order to determine some of the transport parameters, it is not clear whether one model gives significantly better predictions than the other.

Surface Force-Pore Flow Model

The surface force-pore flow (SFPF) model developed by Sourirajan and Matsuura (Matsuura and Sourirajan, 1981; Sourirajan and Matsuura, 1985) is a two-dimensional extension of the finely-porous model. While the finely-porous model considers only axial solute concentration gradients, the SFPF model recognizes that the solute concentration in a RO membrane pore may be a function of radial as well as axial position (Dickson, 1988). The SFPF model assumes (Sourirajan and Matsuura, 1985; Dickson, 1988; Bhattacharyya and Williams, 1992c): (1) water transport through the membrane occurs in pores by viscous flow; (2) solute transport takes place by diffusion and convection in the membrane pores; (3) transport of both water and solute through the membrane pores is determined by interaction forces, friction forces, and chemical potential gradients of the water and solute; (4) the pores of the membrane are cylindrical and run the length of the membrane barrier layer; (5) a molecular layer of pure water is preferentially sorbed on the pore wall; and (6) a potential field controls the solute distribution of the membrane pore.

A balance on the forces acting on the water in the membrane pore shown in Figure 2 (with $\tau = 1$) results in the velocity profile of the solution in the pore as (Sourirajan and Matsuura, 1985)

$$\frac{d^2 u}{dr^2} + \frac{1}{r} \frac{du}{dr} + \frac{1}{\eta} \frac{\Delta P}{\delta} + \frac{1}{\eta} \frac{R_g T}{\delta} (C_P(r)|_{z=\delta} - C_F) \left[1 - \exp\left(\frac{-\phi(r)}{R_g T}\right) \right] - \frac{1}{\eta} [b(r) - 1] X_{sw} C_P(r)|_{z=\delta} u = 0 \quad \text{Eqn. 48}$$

with boundary conditions

$$\left. \frac{du}{dr} \right|_{r=0} = 0 \quad \text{Eqn. 49}$$

$$u(R) = 0. \quad \text{Eqn. 50}$$

Assuming the pure water flow rate through the membrane is described by the Poiseuille equation, the ratio of the water flux to the pure water flux is given by

$$\frac{J_w}{J_{w0}} = \frac{2 \int_0^{R_p} u r dr}{R_p^4 \Delta P}. \quad \text{Eqn. 51}$$

Similarly, a force balance on the solute in the pore results in (Sourirajan and Matsuura, 1985)

$$\frac{C_P(r)|_{z=\delta}}{C_F} = \frac{\exp\left(u(r) \delta \frac{X_{sw}}{R_g T}\right)}{1 + \frac{b(r)}{\exp\left(\frac{-\phi(r)}{R_g T}\right)} \left[\exp\left(u(r) \delta \frac{X_{sw}}{R_g T}\right) - 1 \right]}. \quad \text{Eqn. 52}$$

Equation 52 is similar in form to Equation 39 of the finely-porous model; however, as pointed out by Sourirajan and Matsuura (1985), Equation 39 is valid for the entire pore outlet while Equation 52 represents the permeate concentration only at r at the pore outlet. In addition, the boundary conditions of the SFPF model assume a Maxwell-Boltzmann distribution of solute:

$$C_{pore}(r, 0) = C_F \exp\left(\frac{-\phi(r)}{R_g T}\right) = K_D(r) C_F \quad \text{Eqn. 53}$$

$$C_{pore}(r, \delta) = C_P(r)|_{z=\delta} \exp\left(\frac{-\phi(r)}{R_g T}\right) = K_D(r) C_P(r)|_{z=\delta}; \quad \text{Eqn. 54}$$

that is, the distribution of solute in the membrane is represented in terms of a radially-dependent partition coefficient. The water velocity is also radially dependent for the SFPF model. The total permeate concentration is determined by averaging Equation 52 over the pore outlet (Sourirajan and Matsuura, 1985):

$$C_P = \frac{\int_0^{R_p} C_P(r)|_{z=\delta} u(r) r dr}{\int_0^{R_p} u(r) r dr}. \quad \text{Eqn. 55}$$

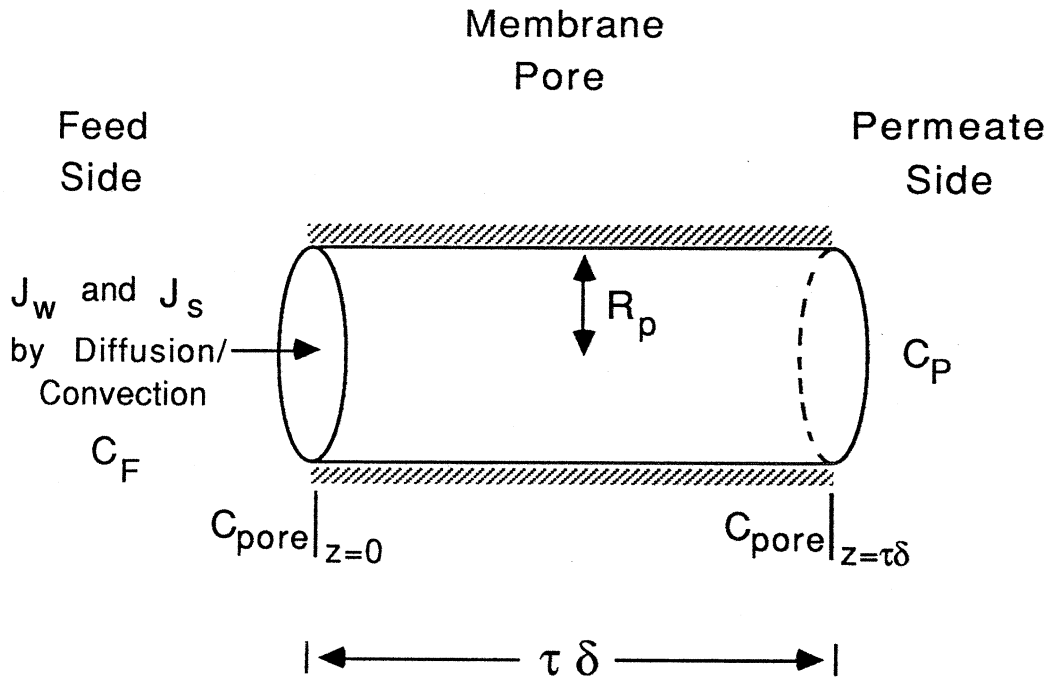


Figure 2. Schematic of a Membrane Pore.

The rejection becomes

$$R = 1 - \int_0^{R_p} \frac{\exp\left(u(r) \delta \frac{X_{sw}}{R_g T}\right) u(r) r}{1 + \frac{b(r)}{\exp\left(\frac{-\phi(r)}{R_g T}\right)} \left[\exp\left(u(r) \delta \frac{X_{sw}}{R_g T}\right) - 1 \right]} dr \div \int_0^{R_p} u(r) r dr . \quad \text{Eqn. 56}$$

The quantity $\phi(r)$ in the water and solute transport equations is given by a coulombic potential function

$$\phi(r) = \frac{\tilde{A}}{R_p - r} \quad \text{Eqn. 57}$$

for ionized solutes where \tilde{A} is a measure of the electrostatic repulsion force between the ionic solute and the membrane; and by a Lennard-Jones potential function

$$\phi(r) = -\frac{\tilde{B}}{(R_p - r)^3} \quad \text{Eqn. 58}$$

for nonionized organic solutes where \tilde{B} is a measure of short range van der Waals forces. The parameters X_{sw} and $b(r)$ are the same as in the finely-porous model; in applications of the SFPP model, b is usually not considered a function of radial pore position.

The transport equations for the SFPP model, expressed in dimensionless form, have been solved using a variety of numerical techniques. Sourirajan and Matsuura (1985) used liquid chromatography techniques in order to determine \tilde{A} or \tilde{B} for a solute and then used trial and error to find the membrane pore radius: R_p was varied until the predicted and measured permeate concentrations were in agreement. Alternatively, if R_p was specified, then \tilde{A} or \tilde{B} was varied to produce agreement in the predicted and measured permeate concentrations. Mehdizadeh and Dickson (1989, 1990) used a similar solution technique. Bhattacharyya et al. (1986) and Jevtitch (1986), using measured pore radius values and one experimental data point for permeate concentration, eliminated the need for trial and error solution of the transport equations by imposing Equation 56 (in differential form) as a condition in the solution of Equation 48 and solving the resulting system of equations by a collocation method; the values of \tilde{A} or \tilde{B} were calculated by this method. Both solution techniques indicated that the SFPP model gave excellent predictions of solute separation for a wide range of inorganics and organics under varying operating conditions. However, for some dilute organics that cause substantial decreases in water flux, Equation 51 does not adequately predict the water flux ratio. The pore radius must be reduced in order to force the predicted and measured water flux ratios into agreement for these systems.

An important modification of the SFPP model has been formulated to recognize that it is more realistic to assume a distribution of membrane pore sizes (Sourirajan and Matsuura, 1985). Mehdizadeh and Dickson (1989) and Mehdizadeh (1990) also pointed out some inconsistencies in the SFPP model similar to those pointed out for the original finely-porous model; they formulated a modified SFPP correcting these conceptual errors. However, although the inclusion of a pore distribution in the SFPP model or the use of Dickson and Mehdizadeh's modified SFPP model is conceptually more correct, it is not immediately obvious that these provide better solute separation predictions.

Charged Membrane Models

Although water transport for charged RO (i.e., nanofiltration) membranes is usually adequately described by the above models, charged RO membrane theories must be used to predict ionic solute separations. These models account for electrostatic effects as well as for diffusive and/or convective flow in order to describe the solute separation. Many charged membrane transport theories have been proposed; two conceptually-important models for solute transport are discussed below.

Donnan Equilibrium Models

Donnan equilibrium models assume that a dynamic equilibrium is established when a charged membrane is placed in a salt solution (Bhattacharyya and Cheng, 1986; Bhattacharyya and Williams, 1992c). The counter-ion of the solution, opposite in charge to the fixed membrane charge (typically carboxylic or sulfonic groups), is present in the membrane at a higher concentration than that of the co-ion (same charge as the fixed membrane charge) because of electrostatic attraction and repulsion effects. This creates a Donnan potential which prevents the diffusive exchange of the counter-ion and co-ion between the solution and membrane phase. When a pressure driving force is applied to force water through the charged membrane, the effect of the Donnan potential is to repel the co-ion from the membrane; since electroneutrality must be maintained in the solution phase, the counter-ion is also rejected, resulting in ionic solute separation.

A Donnan equilibrium model utilized by Bhattacharyya and Cheng (1986) described the distribution coefficient between a negatively-charged membrane and the solution phase of a salt M_nN_m which ionizes to M^{m+} and N^{n-} as

$$K = \frac{C_{im}}{C_{Fi}} = \left[\left(\frac{n C_{Fi}}{C_m^*} \right)^n \left(\frac{\gamma}{\gamma_m} \right)^{m+n} \right]^{\frac{1}{m}} \quad \text{Eqn. 59}$$

and then approximated the solute rejection as

$$R = 1 - K \quad \text{Eqn. 60}$$

The model correctly predicted that the solute rejection was a function of membrane charge capacity (C_m^*), ion feed concentration (C_{Fi}), and ion charge (m, n). However, this model does not take into account solute diffusive and convective fluxes which may also be important in charged membrane separations.

Extended Nernst-Planck Model

Lakshminarayanaiah (1965, 1969), Dresner (1972), and Dresner and Johnson (1980) have described the use of extended Nernst-Planck equations for the prediction of solute ion fluxes. The general form of the equation is given by

$$J_{is} = J_w C_{im} + z_i C_{im} \frac{F\tilde{E}}{R_g T} - D_{im} \frac{d C_{im}}{dz} - C_{im} D_{im} \frac{d(\ln \gamma_{im})}{dz} \quad \text{Eqn. 61}$$

The first term in Equation 61 represents the solute flux contribution due to convection, the second term accounts for solute flux due to the Donnan potential, and the last two terms describe solute transport due to diffusion. Dresner (1972) has shown that the extended Nernst-Planck model correctly predicts the trends expected for ionic solute rejection, including conditions under which a negative rejection is obtained.

Other RO Membrane Transport Models

Several other transport models for RO membranes have also been proposed in the literature. Soltanieh and Gill (1981) and Sourirajan and Matsuura (1985) discussed the relative free energies of membrane-ion interactions and the relation of these to membrane selectivity. Garcia and Medina (1989) reported some success in the use of dimensional analysis to correlate experimental RO membrane data. Mason and Lonsdale (1990) presented the general statistical-mechanical theory of membrane transport; they pointed out that most RO membrane transport models (solution-diffusion, diffusion-convection, etc.) could be derived from statistical-mechanical theory. Bitter (1991) also developed a general model based on the solution-diffusion mechanism using Maxwell-Stefan equations to calculate diffusive transport and Flory-Huggins equations to calculate solubility of species in the membrane. Bitter indicated that the procedure he used should be applicable to almost all membrane systems; however, some of the solute, solvent, and membrane properties needed in the model are difficult to obtain.

Thiel and Lloyd (1990) used the extended Stefan-Maxwell equations to describe total flux (solute plus solvent) of aqueous-organic solutions through membranes; their model indicated that water flux reduction was in part due to frictional effects caused by the organic. The model had the form

$$N_T = \frac{A \{ \Delta P - [\pi(X_F) - \pi(X_P)] \}}{1 + W_s X_P}, \quad \text{Eqn. 62}$$

where the term $W_s X_P$ was described as a solute-membrane friction term. Connell and Dickson (1988) had previously used a similar empirically-derived relationship to successfully describe reduction in water flux for aqueous-organic systems. Rautenbach and Gröschl (1990a, 1991) were also able to adequately describe fluxes for both water and organic solute by modifying the solution-diffusion model; they assumed the water and organic content of the membrane was constant.

Williams (1989) used an adsorption resistance term to describe flux drop caused by dilute organic solutes with a RO membrane; he assumed the organics adsorbed on the membrane and so caused more resistance to water flow through it. The model was given as

$$J_w = \frac{\Delta P - \Delta \pi}{R_m + R_{Ads}}, \quad \text{Eqn. 63}$$

where R_m is the membrane resistance and R_{Ads} is the resistance due to solute adsorption. Bhattacharyya and Madadi (1988), Deshmukh (1989), and Kothari (1991) also used similar expressions to describe water fluxes for organic solutes that adsorbed on the RO membranes they studied. Forms of Equation 63 have also been applied extensively to describe ultrafiltration membranes (Cheryan, 1986; Kulkarni et al., 1992; Nakatsuka and Michaels, 1992; Bhattacharjee and Bhattacharya, 1992a, 1992b).

Concentration Polarization

Concentration polarization is the term used to describe the accumulation of rejected solute at the surface of a membrane so that the solute concentration at the membrane wall is much higher than that of the bulk feed solution. As water passes through the membrane, the convective flow of solute to the membrane surface is much larger than the diffusion of the solute back to the bulk feed solution; as a result, the concentration of the solute at the membrane wall increases. This is shown

schematically in Figure 3. Reviews of concentration polarization are given by Matthiasson and Sivik (1980), Gekas and Hallstrom (1987), Rautenbach and Albrecht (1989), and Bhattacharyya and Williams (1992c).

Possible negative effects of concentration polarization include: (1) decreases in water flux due to increased osmotic pressure at the membrane wall; (2) increases in solute flux through the membrane because of increased concentration gradient across the membrane; (3) precipitation of the solute if the surface concentration exceeds its solubility limit, leading to scaling or particle fouling of the membrane and reduced water flux; (4) changes in membrane separation properties; and (5) enhanced fouling by particulate or colloidal materials in the feed which block the membrane surface and reduce water flux. The extent of concentration polarization can be reduced by promoting good mixing of the bulk feed solution with the solution near the membrane wall. Mixing can be enhanced through membrane module optimization of turbulence promoters, spacer placement, hollow fiber diameter, etc. or by simply increasing axial velocity to promote turbulent flow.

Concentration polarization complicates the modeling of membrane systems because it is very difficult to experimentally determine the solute wall concentration (C_w); the wall concentration is necessary since it and not the bulk feed concentration (C_F) is used in most RO transport models. For very high feed flow rates, enough mixing near the membrane surface occurs so that the wall concentration can be assumed equal to the bulk concentration (that is, the boundary layer thickness $\zeta(z)=0$). However, at lower feed flow rates, the difference between the wall and bulk concentration can be substantial and so the wall concentration must be calculated.

The Navier-Stokes diffusion-convection equation is solved in order to calculate the wall concentrations. For example, for flow over a flat sheet membrane, the concentration profile is given by (Bhattacharyya and Williams, 1992c)

$$U \frac{\partial C}{\partial z} + V \frac{\partial C}{\partial y} - D_{sw} \left(\frac{\partial^2 C}{\partial z^2} + \frac{\partial^2 C}{\partial y^2} \right) = 0 \quad \text{Eqn. 64}$$

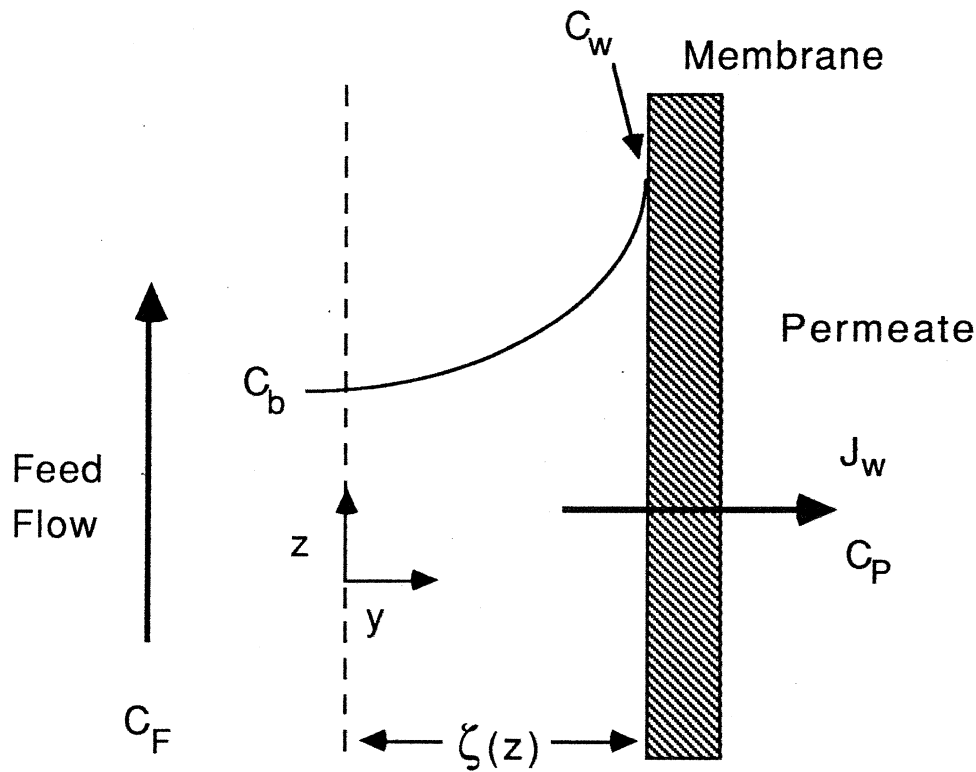
with boundary conditions

$$C(0, y) = C_F \quad \text{Eqn. 65}$$

$$\frac{\partial C(z, 0)}{\partial y} = 0 \quad \text{Eqn. 66}$$

$$D_{sw} \frac{\partial C [z, \zeta(z)]}{\partial y} = V_w \{ C [z, \zeta(z)] - C_P(z) \} \quad \text{Eqn. 67}$$

$$C [z, \zeta(z)] = C_w(z) = \frac{C_P(z)}{1 - R} \quad \text{Eqn. 68}$$



- C_F = initial feed concentration
- C_b = bulk feed concentration
- C_w = wall concentration

Figure 3. Concentration Polarization Concentration Profile.

where the rejection in Equation 68 is calculated using the wall concentration; it can be found for a case with no concentration polarization and negligible recovery. Equations 64, 65, 66, 67, and 68 along with appropriate velocity expressions $U(z,y)$ and $V(z,y)$ can be solved numerically for the wall concentrations (Jevtitch, 1986; Back, 1987; Bhattacharyya et al., 1990). If the boundary layer shown in Figure 3 is assumed to be stagnant and not change along the channel length ($\zeta(z) = \zeta$), Equation 64 reduces to

$$V_w \frac{\partial C}{\partial y} = D_{sw} \frac{\partial^2 C}{\partial y^2} \quad \text{Eqn. 69}$$

which can be integrated to

$$\frac{C_w - C_P}{C_F - C_P} = \exp\left(\frac{V_w \zeta}{D_{sw}}\right); \quad \text{Eqn. 70}$$

this is the widely-applied film theory developed by Brian (Brian, 1966; Bhattacharyya and Williams, 1992c). The film thickness ζ can be related to the Sherwood number for the membrane system; Gekas and Hallstrom (1987) have reviewed correlations for the Sherwood number for various membrane geometries.

Description of Operating Variable Effects

Factors affecting RO membrane separations include: feed variables such as solute concentration, temperature, pH, and pretreatment requirements; membrane variables such as polymer type, module geometry, and module arrangement; and process variables such as feed flow rate, operating pressure, operating time, and water recovery (Bhattacharyya et al., 1992). Selected generalized curves illustrating the effects of some of these variables are shown in Figure 4 for noninteracting solutes. Water flux, for example, is shown to increase linearly with applied pressure; this behavior is predicted by most of the RO transport models. Water flux also increases with temperature, as would be expected, since the water diffusivity in the membrane increases and the water viscosity in the membrane decreases with temperature; the increase in water flux can usually be described by an Arrhenius temperature dependence of the water permeability constant or by water viscosity changes (Sourirajan and Matsuura, 1985; Dickson, 1988; Mehdizadeh et al., 1989; Mehdizadeh and Dickson, 1991). In addition, water flux is greater at higher feed flow rates (high feed velocities over the membrane surface) since this minimizes concentration polarization.

Water flux decreases with increasing feed solute concentration since the higher concentrations result in larger osmotic pressures (and so a smaller driving force across the membrane). This behavior is also predicted by most of the transport models. Water flux can also gradually decrease over operating time (measured in days or months of operation) because of compaction (mechanical compression) or other physical or chemical changes in membrane structure. These changes are usually described with empirical relations (Bhattacharyya et al., 1992).

Solute rejection usually increases with pressure (up to an asymptotic value) since water flux through the membrane increases while solute flux is essentially unchanged when pressure is increased; however, rejection of some organics with strong solute-membrane interactions decreases with pressure (Bhattacharyya and Williams, 1992c). Rejection of solute remains constant or decreases with increasing temperature depending on the relative increases of water and solute diffusivities in the membrane. For most simple inorganic systems (such as NaCl, Na₂SO₄, etc.), feed pH does not significantly affect water or solute fluxes. However, for ionizable organics, rejection is a strong function of feed pH: the organic is usually much more highly rejected when it is ionized (Sourirajan and Matsuura, 1985; Bhattacharyya et al., 1987; Dickson, 1988; Bhattacharyya and Williams, 1992a).

Feed water quality is also important since particulates, colloids, or precipitates present in the feed can cause fouling of a membrane by depositing on its surface, resulting in a substantially reduced water flux. Bacteriological growth can also occur in RO membrane modules, forming bacterial layers that decrease water flux and, in some cases, degrade the membrane polymer.

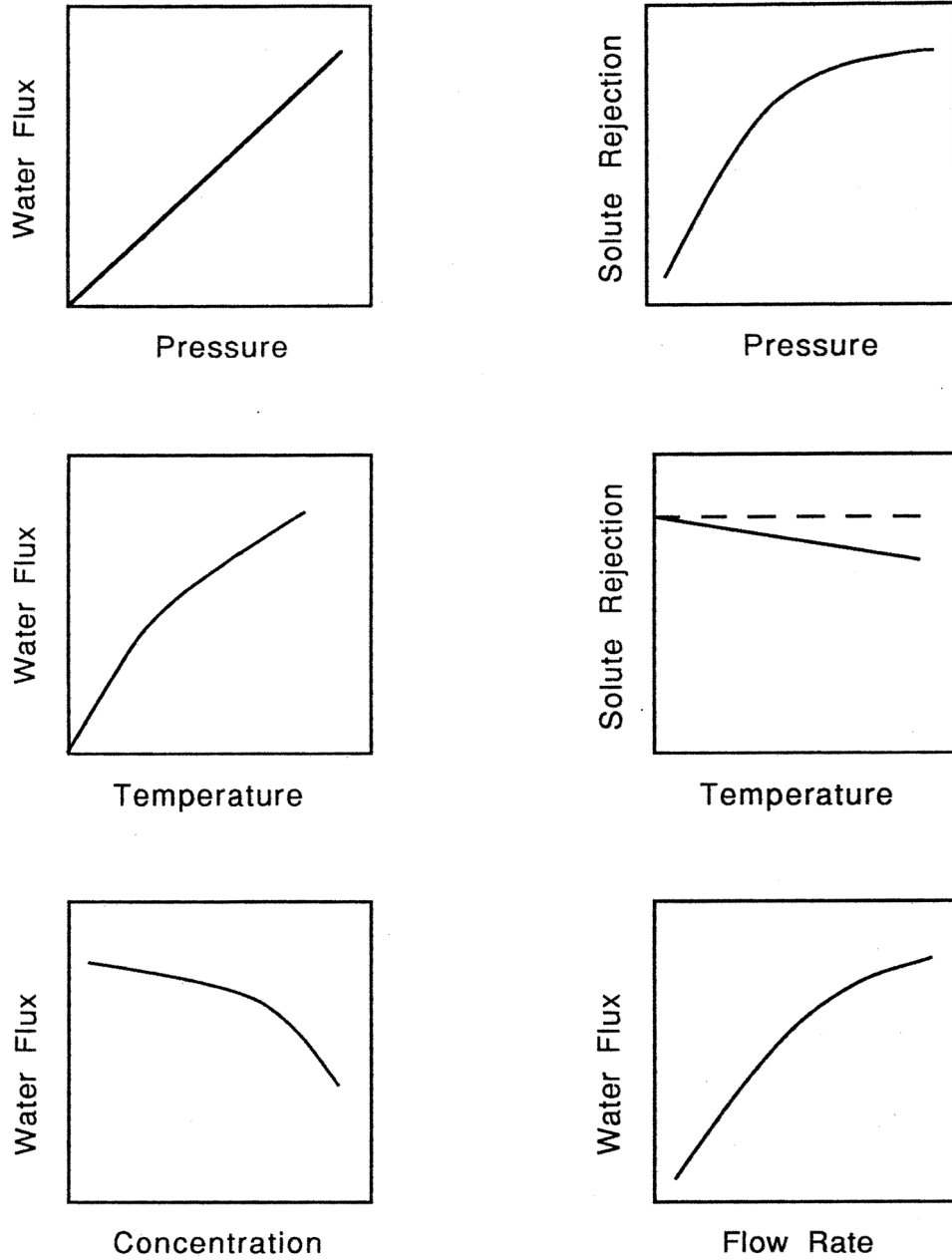


Figure 4. Effects of Variables on RO Separations (Adapted from Riley, 1990).

Pretreatment methods such as filtration, flocculation, disinfection as well as others are used to remove or neutralize potential fouling contaminants in the feed stream. These methods are thoroughly discussed in Bhattacharyya et al. (1992). It should be pointed out, however, that water flux drops caused by some dilute organic solutes cannot be viewed as simple fouling since for these it is membrane-solute interactions that cause the flux decreases and not particulate deposition, scaling, or two phase formation on the membrane surface.

Water-Solute-RO Membrane Interactions

The interactions between water, solutes, and the membrane are the most important factors in RO separations. As a result, even though the interactions can be very difficult to study, these have received considerable attention. For example, Strathmann and Michaels (1977) examined water sorption by and water permeability of several different polymer membranes. They concluded that to maximize water permeability through the membrane the polymer should have a high water sorption and a small water cluster size in the polymer matrix; that is, the water should be molecularly dispersed in the membrane and not hydrogen bonded to each other in clusters in order to enhance its diffusivity through the membrane. Luck (1984, 1987) indicated that water in efficient RO membranes has a different structure and forms weaker hydrogen bonds with one another than in liquid water due to interactions with the membrane polymer. He proposed that in these membranes the hydration layer is composed of clusters of water molecules too small to dissolve ions and so the ions do not partition well into the membrane, resulting in high rejections. Also, since the hydration layer forms weaker hydrogen bonds with each other, the water diffusion activation energies in the membrane are lower and so water fluxes higher than in membranes which contain large clusters of water molecules that are more strongly hydrogen-bonded to one another. Differences in water structure and bonding in RO membranes have also been discussed by Burghoff and Pusch (1976) and Pusch (1990).

Solute-membrane interactions have been both measured and calculated. Sourirajan and Matsuura (1985), Jiang et al. (1989), and Gao and Bao (1989) have used liquid chromatography with the membrane polymer as the column packing in order to directly measure inorganic and organic solute-membrane interfacial parameters such as equilibrium distribution coefficient, Gibbs free energy, and surface excess for a large number of different polymers. Sourirajan and Matsuura (1985), Bhattacharyya et al. (1986), and Mehdizadeh and Dickson (1989) have also used the SFPF model in order to calculate solute-membrane interaction forces (coulombic or van der Waals). Jiang and Jiayan (1990) characterized interactions of organic solutes with polybenzimidazole membranes using quantum chemistry calculations, liquid chromatography, and IR spectroscopy. They determined that hydrogen bonding was the main interaction force between the solutes (benzyl alcohol and 1,4-dioxane) and the membrane. They also concluded that benzyl alcohol rejection was substantially lower than that of dioxane because the alcohol had much stronger interactions with the membrane; as a result, it could substitute for water in the membrane and so more easily transport through. The dependence of organic rejection on its extent of hydrogen bond formation with the membrane has been suggested previously (Kesting and Eberlin, 1966; Duvel and Helfgott, 1975; Sourirajan and Matsuura, 1985). Sourirajan and Matsuura (1985) also indicated that organic hydrogen bonding with RO membrane polymers might reduce water flux through the membrane. Burghoff et al. (1980) found that sorption of phenol by cellulose acetate membranes decreased the water content of the membrane.

Cheng et al. (1991) considered the effects of small halocarbons (chloroform, bromoform, and carbon tetrachloride) on several RO membranes. They found that the organics caused a reduction in

the membranes' void spaces; this represents a decrease in water content of the membrane, possibly caused by substitution of the water in the membrane with organic. Analysis of partition coefficients indicated that the organics were significantly sorbed into the membrane. Several other studies have also shown that some organic solutes (even dilute solutions) such as chloro- and nitrophenols and polynuclear aromatic hydrocarbons interact with RO membranes, substantially changing water flux characteristics (Bhattacharyya et al., 1987; Bhattacharyya and Madadi, 1988; Bhattacharyya and Kothari, 1991; Bhattacharyya and Williams, 1992a). These studies indicated that adsorption of the solute on the membranes was related to the water flux drops observed.

Murphy (1991) found that sorption of aqueous nonionized phenol solutions onto cellulose acetate could be described by a Langmuir isotherm; he postulated that the phenol formed hydrogen bonds with the polymer. Deshmukh (1989) and Williams et al. (1990) discussed adsorption studies of chloro- and nitrophenols on polyamide membranes. They reported adsorption of nonionized solutes on/in membranes placed in aqueous solution could also be described by Langmuir isotherms. The relative quantities of solute adsorbed was in the order 2,4,6-trichlorophenol > 2,4-dichlorophenol > 2,4-dinitrophenol > 2-chlorophenol. However, the adsorbate solution pH played an important role. When the solutes were ionized ($\text{pH} > \text{pK}_a$), membrane adsorption was substantially lower, indicating the ionized organic solutes did not interact as strongly with the membrane. Also, the quantities of adsorbed solute (nonionized conditions) decreased when membrane adsorption from 30% methanol-water solutions was studied. It was concluded that the methanol-water solution had a higher affinity for the solutes and so these adsorbed less in the membrane. Madadi (1987) had previously noted that water flux drops caused by dilute organics such chloro- and nitrophenols were lower when the solutes were in alcohol-water solutions, indicating organic-membrane interactions were not as strong when alcohols were present in the feed solutions.

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