

# OVERVIEW OF REVERSE OSMOSIS FOR CHEMICAL ENGINEERS

## PART 1: FUNDAMENTALS OF MEMBRANE MASS TRANSFER

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**Abstract** Reverse osmosis (RO) has become a standard unit operation in Chemical Engineering. This separation process can be used for a wide variety of applications including: desalination of sea water, treatment of industrial wastes, concentration of food products, and recovery of value materials from solution mixtures. In order to best utilize RO it is necessary to have a fundamental understanding of the process so that the optimum design can be reached. In this first part of a two-part series, the fundamental aspects of the RO process are reviewed, several transport models are summarized and the design equations necessary for scale up are presented. The emphasis is to provide a simple, practical, and yet comprehensive summary of the most relevant information that will be needed by a chemical engineer trying to apply reverse osmosis membranes to specific applications.

**چکیده** فرآیند اسمز معکوس، جزء عملیات واحد متداول (جداسازی) در مهندسی شیمی است که میتواند کاربردهای متنوعی مانند نمکزدائی از آب دریا، تصفیه پسابهای صنعتی تغلیظ مواد غذایی و بازیابی مواد با ارزش از محلولها و مخلوطها داشته باشد. برای استفاده از این فرآیند، طراحی مناسب یک واحد، لازم است از مفاهیم اصول آن درک کافی داشت. این مقاله که اولین بخش از یک مجموعه دو قسمتی است به مرور مفاهیم اصولی فرآیند اختصاص دارد. چکیده چند مدل مختلف انتقال و معادلات لازم برای افزایش مقیاس تولید ارائه شده است. تاکید این مقاله بر ارائه یک خلاصه ساده، عملی و قابل فهم از مهمترین اطلاعات مورد نیاز برای کاربرد این فرآیند توسط یک مهندس شیمی میباشد.

### INTRODUCTION

Although invented about 30 years ago on the lab scale, the reverse osmosis (RO) separation process has become a major unit operation in Chemical Engineering. Today, this membrane separation process has found a wide variety of applications as in producing potable water and agricultural water by desalination of seawater and brackish water industrial pure water, industrial and municipal wastewater treatment, in chemical, petrochemical, and textile industries, and in food and pharmaceutical industries to name a few [1-3].

A good understanding of the fundamentals of the membrane transport is needed in order to properly describe and predict membrane performance, and to design practical RO units. It is a challenge to Chemical Engineers

to provide these models and develop useful methods of design. The purpose of this paper is to provide the reader with an overview of the fundamental aspects of reverse osmosis. The emphasis is to provide a simple, practical, and yet comprehensive summary of the most relevant information that will be needed by a chemical engineer trying to apply reverse osmosis membranes to specific applications. A detailed summary of several transport models is given for the interested reader.

Covered in this first part of a two-part series is information on osmotic pressure, the driving forces for mass transfer in membranes, concentration polarization, the physicochemical criteria for separation, transport models for permeation in membranes and the design equations needed for scale up. The

second part of this series will examine the ability of transport models to describe and predict membrane performance. Most of the information on modelling membrane transport is restricted to single solute systems. How these models can be used to describe the more difficult problem of mixed solute systems will be discussed in the second paper.

### 1. Membrane Performance

Typically, membrane performance is characterized in terms of flux and separation as illustrated in Figure 1. Flux is the rate of material transported per unit membrane area and separation is the relative change in concentration from the feed stream to the permeate stream.

Separation (which is called equivalently rejection and retention in some references),  $f$ , is defined in terms of the feed and permeate molal concentrations,  $m_{A1}$  and  $m_{A3}$ , respectively [5]:

$$f = (m_{A1} - m_{A3}) / m_{A1} \quad (1)$$

For moderately dilute solutions, the molal concentration,  $m_{Ai}$ , can be approximated by the molar concentration,  $C_{Ai}$ , and Equation (1) can be rewritten as:

$$f = (C_{A1} - C_{A3}) / C_{A1} \quad (2)$$

Alternatively, separation can be defined in terms of the concentration of the boundary solution near the membrane surface,  $C_{A2}$ . The separation based on the boundary layer concentration,  $f'$ , can be written as:

$$f' = (C_{A2} - C_{A3}) / C_{A2} \quad (3)$$

The separation calculated in this manner represents the theoretical separation that would be measured with perfect mixing on

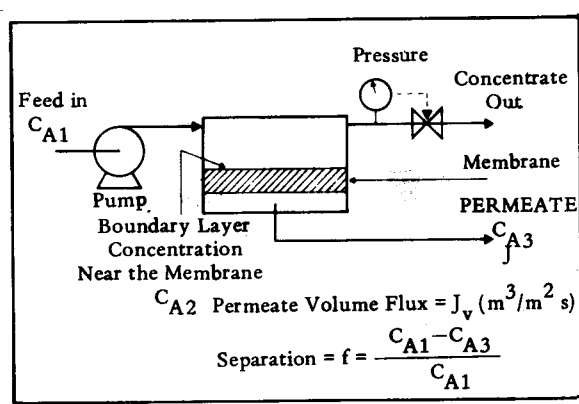


Figure 1. Reverse osmosis performance.

the high pressure side of the membrane. The advantage of using  $f'$  for modelling purposes is that  $f'$  is function of the concentrations that are adjacent to the membrane surface. The  $f$  and  $f'$  values can be related by considering the concentration polarization phenomenon as described below.

### 2. Osmotic Pressure

When an ideal semi-permeable membrane (one that is permeable to solvent but not to solute) is placed between two compartments, one containing pure solvent and the other containing a solution (solvent plus solute), the solvent passes through the membrane to the solution side. This phenomenon is called "osmosis" (see Figure 2). Transport occurs due to the chemical potential driving force which is caused by the presence of the solute. The exact pressure that must be applied to the solution side to stop the solvent flux is called the "osmotic pressure". In reverse osmosis, a pressure greater than the osmotic pressure is applied to the solution to reverse the flow and drive solvent from the solution side to the pure solvent side; hence, the name reverse osmosis (see Figure 2). To model the flux through a membrane, the influence of the osmotic pressure driving force must be considered.

For a real membrane, some solute exists in the permeate and therefore the osmotic pressure of the solution on each side of the membrane must be considered. An effective pressure driving force across the membrane can be defined as the applied pressure difference minus the osmotic pressure difference. For most models, the water flux is considered to be proportional to the effective pressure driving force.

Osmotic pressure is a thermodynamic property (a colligative property) of a solution and as such values can be found in various reference books [5, 6]. The osmotic pressure of a solution at position  $i$ ,  $\pi_i$ , is related to the mole fraction of the solvent,  $X_B$ , as [7]:

$$\pi_i = -(RT/V_B) \ln X_B \quad (4)$$

For dilute systems, Equation 4 simplifies to the van't Hoff Equation [7]:

$$\pi_i = C_{Ai} RT \quad (5a)$$

where  $C_{Ai}$  is the molar concentration at position  $i$ . If the solute dissociates then each ion contributes to the osmotic pressure so that for a completely dissociated salt  $M\nu^+X\nu^-$ , the osmotic pressure is:

$$\pi_i = (\nu^+ + \nu^-) C_{Ai} RT \quad (5b)$$

Therefore, the osmotic pressure difference across a membrane,  $\Delta\pi$ , is related linearly

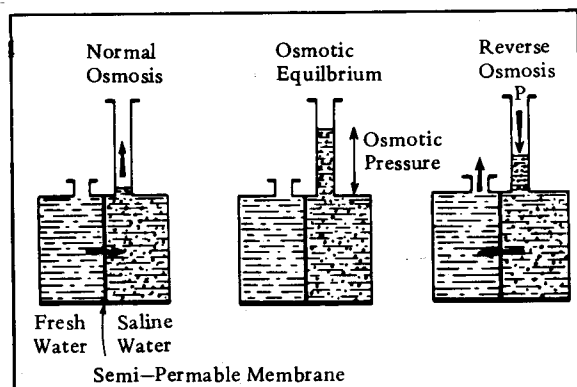


Figure 2. The principle of the reverse osmosis process (with permission from reference [4]).

to the concentration difference,  $(C_{A2}-C_{A3})$ . The above two equations are useful, but it is preferable to use experimental data on osmotic pressure if the information is available.

### 3. Driving Forces for Transport

In general, several driving forces are possible in membrane transport. The main driving forces are pressure, concentration, electrical potential, and temperature each of which primarily influences the flux of solvent, solute, electrical current and thermal energy, respectively. In addition to the primary effects, each of the driving forces has a cross influence on the other fluxes. For instance the pressure driving force can cause a flux of current, called the streaming current [8].

In reverse osmosis systems, the only driving forces of interest are pressure and concentration which lead to flux of solvent and solute, respectively (see Figure 3). The cross influence of solute concentration driving force on solvent flux is represented by the osmotic pressure term in the solvent flux equation. For high separation membranes, the cross influence of pressure driving force on solute flux is often small and is therefore neglected; When it is included this effect is described by the Staverman (or reflection) coefficient [9].

Driving Force \ Flux	Pressure Gradient	Concentration Gradient
Solvent Flow	Solvent Permeability	Osmosis
Solvent Flow	Ultrafiltration	Diffusion

Figure 3. Fluxes and driving forces in reverse osmosis.

The solvent flux equation, written here for both volume flux,  $J_v$ , and molar flux of solvent,  $N_B$ , indicates that flux is directly proportional to the effective pressure driving force [5]:

$$N_B = J_v C = A(\Delta P - \Delta \pi) \quad (6)$$

where  $A$  is the appropriate proportionality constant.

#### 4. Concentration Polarization

When solute is rejected by the membrane, the solute concentration near the membrane surface increases. The build-up in concentration in this boundary layer region is referred to as "concentration polarization". The polarization can be described by film theory [10]. At steady state, the flux of solute to the membrane,  $(N_A + N_B) C_A/C$ , the flux of solute through the membrane,  $N_A$ , and the solute back diffusion,  $-D_{AB} dC_A/dx$ , are balanced as illustrated in Figure 4. Mathematically:

$$N_A = (N_A + N_B) C_A/C - D_{AB} dC_A/dx \quad (7)$$

which is a form of Fick's first law [10]. Solving this equation with appropriate boundary conditions [5, 11] gives:

$$C_{A2} = C_{A3} + (C_{A1} - C_{A3}) \exp(N_T/kC) \quad (8)$$

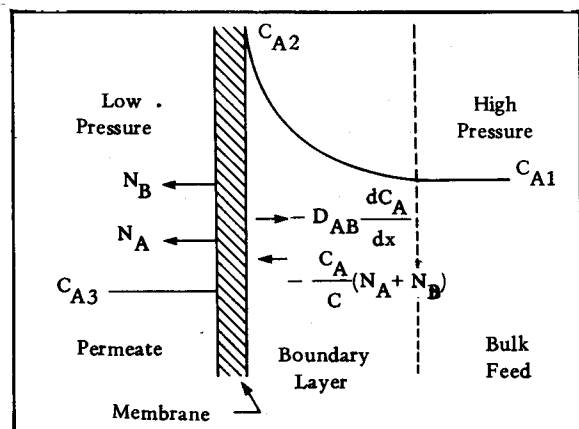


Figure 4. Concentration polarization at the high pressure surface of a reverse osmosis membrane.

where  $N_T$  is the total molar flux of solute and solvent through the membrane, and  $C_{A1}$ ,  $C_{A2}$ , and  $C_{A3}$  are the feed, boundary layer, and permeate concentrations, respectively. As the mixing on the high pressure side of the membrane is increased, the mass transfer coefficient,  $k$ , increases and Equation 8 predicts that concentration polarization decreases ( $C_{A2}$  decreases and approaches  $C_{A1}$ ).

Some authors choose to ignore the influence of concentration polarization by claiming that if the mixing is sufficiently thorough, the boundary layer concentration approaches the bulk concentration. This may not be the case in large scale systems or even in many laboratory scale apparatus. Therefore, the best method is to specifically account for concentration polarization by using Equation 8 or some equivalent method.

Other approaches have been used to describe the concentration polarization layer more accurately (see for instance, [12]). However, for most practical purposes, Equation 8 is sufficiently accurate. For each of the models presented below, the original reference can be checked to determine how the authors modelled concentration polarization.

The mass transfer coefficient is a function of feed flow rate, cell geometry, and solute system. Generalized correlations of mass transfer, which have been used by several authors [5, 11, 13-15], suggest that the Sherwood number,  $N_{Sh}$  is related to the Reynolds,  $N_{Re}$ , and Schmidt,  $N_{Sc}$ , numbers as:

$$N_{Sh} = a N_{Re}^b N_{Sc}^{1/3} \quad (9)$$

where  $a$  and  $b$  are parameters that can be determined experimentally.

For a fixed feed flow rate and cell geometry, Equation 9 indicates that  $k$  varies as a

function of the diffusivity of the solute to the 2/3 power. Writing Equation 9 with respect to a reference solute at the same experimental conditions gives:

$$k = k_{\text{ref}} (D_{\text{AB}}/D_{\text{AB,ref}})^{2/3} \quad (10)$$

If  $k$  is known for a reference solute, then  $k$  for any other solute can be estimated using Equation 10 if the diffusivities of the solute and reference solute are known.

## 5. Membrane Structure

In order to facilitate the description of the various membrane models, a brief discussion of membrane structure is included here. The inquiry into the exact relationship between membrane structure and performance is an on-going concern (see for instance references [15, 17] and the present discussion is limited to some of what is known about typical synthetic membranes.

The success of the reverse osmosis process is due in part to the development of the asymmetric membrane. An asymmetric membrane has a relatively dense surface layer supported by a porous layer underneath. Such a structure greatly reduces the resistance to flow through the membrane compared to a homogeneous dense membrane of the same overall thickness. The asymmetric structure is a direct consequence of the casting procedure used. When a polymer solution is cast on a flat surface, the evaporation of the solvent produces a surface skin. Subsequent gelation in cold water fixes the structure; the porous substructure is formed by the replacement of solvent by the nonsolvent water. Scanning electron microscope (SEM) examination of membranes made in this manner [18] indicates that three layers exist: a relatively dense surface skin, a transition layer, and an

open porous support layer. The transition layer is intermediate in both density and position with respect to the other two layers. Most of the resistance to mass transfer through the membrane exists in the surface skin. Therefore, it may be assumed that the performance of the membrane is dependent primarily on the chemical nature, thickness, and structure of the surface skin.

Thin film composite membranes have a similar structure to asymmetric membranes described above except that the porous support is fabricated first from one polymer material (chosen for mechanical strength and chemical resistance) and a thin film of a different polymer is coated (often by interfacial polymerization) on the porous substrate. The coated film is thin to increase flux and made from a polymer that has good separation characteristics.

For the skin layer, the basic question is whether it is porous. Membranes with pores sufficiently large that they can be seen with a SEM are usually considered to be ultrafiltration membranes. These membranes are clearly porous. As the pore size becomes progressively smaller, there is no clear point at which the pores disappear. With the technology available today, the existence or absence of pores in RO membranes can not be determined.

With this uncertainty in the membrane structure it is necessary to consider models that make no assumptions about membrane structure and mechanistic models that assume a membrane structure.

## TRANSPORT MODELS

The general purpose of a membrane mass transfer model is to relate the performance (usually expressed in terms of flux of solvent

and solute) to the operating conditions (usually expressed in terms of pressure and concentration driving forces). In the model, some coefficients (transport coefficients) emerge that must be determined based on experimental data. The success of a model can be measured in terms of the ability of the model to describe mathematically the data with coefficients that are reasonably constant over the range of operating conditions. Ultimately the model plus the now known transport coefficients can describe the performance of the membrane over a wide range of operating conditions. This ability to predict the performance is the true power of a transport model. Combined with a research program in membrane making this can lead to better design criteria for tailor making membranes and combined with a process design program can lead to a more logical scaleup procedure for reverse osmosis systems.

The flux of solute and solvent through a membrane are related to the permeate concentration by material balance as:

$$C_{A3} = C N_A / (N_A + N_B) \quad (11)$$

At moderately low concentrations, where  $N_B \gg N_A$  and the difference between molal and molar concentration may be ignored ( $C_{A1} = m_{A1}$ ), Equations 3 and 11 can be combined to give:

$$f' = 1 - \frac{C N_A}{C_{A2} N_B} \quad (12)$$

Equation 12 is used frequently in the derivation of the following models.

### 1. Mechanism Independent Transport Models

This section overviews models which are independent of the mechanism of transport. These models are based on the theory of irreversible thermodynamics.

### 1. 1. Irreversible Thermodynamics-Phenomenological Transport Relationship.

Premises of the model. In the absence of any knowledge of the mechanism of transport or the nature of the membrane structure, it is possible to apply the theory of irreversible thermodynamics (IT) to membrane systems [19]. In IT, the membrane is treated as a "black box". Models stating the relationship between forces acting on the system and the flux of material through the membrane are formulated. For systems that are not far from equilibrium, IT suggests reasonable choices for forces and fluxes. The phenomenological relationships are manageable ways of expressing the relationships between the observed fluxes and the applied forces.

#### Mathematical formulation of the model.

Onsager [20] suggested that the fluxes and forces could be expressed by the following linear equations:

$$J_i = L_{ii} F_i + \sum_{i \neq j} L_{ij} F_j \quad \text{for } i=1, \dots, n$$

where the fluxes,  $J_i$ , are related to the forces,  $F_j$ , by the phenomenological coefficients,  $L_{ij}$ . For membrane systems, the driving forces can be related to the pressure and concentration differences across the membrane, and the fluxes are solvent and solute permeate fluxes. This equation can be simplified by assuming that cross coefficients are equal [20]:

$$L_{ij} = L_{ji} \quad \text{for } i \neq j$$

The above Onsager reciprocal relationship (ORR) is valid when the system is close to equilibrium, the linear laws (Equation 13) are valid, and the correct choice of fluxes and forces has been made. For systems that are

far from equilibrium, as is often the case in reverse osmosis, Equation 14 may not be correct. The validity of the Onsager reciprocal relations has been discussed by Soltanieh and Gill [21].

Kedem and Katchalsky [19] used Equations (13) and (14) to derive what are known as the phenomenological transport equations:

$$J_v = \ell_p (\Delta P - \sigma \Delta \pi) \quad (15)$$

$$N_A = \omega \Delta \pi + (1 - \sigma) (C_{AM})_{\ln} J_v \quad (16)$$

where the adjustable parameters  $\ell_p$ ,  $\omega$ , and  $\sigma$  are simple functions of the original phenomenological coefficients,  $L_{ij}$ . Equation 15 is similar to Equation (6) with the addition of the reflection coefficient,  $\sigma$ , as originally proposed by Staverman [9]. The Staverman coefficient acts to describe the effect of the pressure driving force on the flux of solute. For a high separation membrane this effect is small and  $\sigma$  approaches 1.0 so that Equation 15 becomes equivalent to Equation 6. For a low separation membrane the solute is significantly carried through the membrane by solvent flux and  $\sigma$  approaches 0.0 so that the osmotic driving force becomes unimportant in Equation 15. Thus the Staverman (or reflection) coefficient represents the relative permeability of the membrane to the solute.

Pusch [22] has shown that Equation 16 can be rewritten to relate separation,  $f'$ , and flux,  $J_v$ , as:

$$\frac{1}{f'} = \frac{1}{\sigma} + \left( \frac{\ell_\pi}{\ell_p} - \sigma^2 \right) \left( \frac{\ell_p}{\sigma} \right) \pi_2 \left( \frac{1}{J_v} \right) \quad (17)$$

The above equation predicts a linear relationship between  $1/f'$  and  $1/J_v$ . The osmotic permeability,  $\ell_\pi$ , is related to  $\omega$  as:

$$\omega = (\ell_\pi / \ell_p - \sigma^2) (C_{AM})_{\ln} \ell_p \quad (18)$$

The parameters in the model are the solvent and osmotic permeabilities,  $\ell_p$  and  $\ell_\pi$ , and the reflection coefficient,  $\sigma$ . These parameters can be determined for a given solute and membrane by applying Equations 15 and 17 simultaneously using data collected at different operating conditions.

For reverse osmosis systems, the phenomenological transport equations have only been used to a limited extent for describing membrane transport for two reasons. First, the concentration differences across the membrane are often large enough that the linear laws are not valid. As a result the  $L_{ij}$  coefficients are concentration dependent [20]. However, for many systems, the coefficients  $\ell_p$ ,  $\ell_\pi$ , and  $\sigma$  are nearly constant provided that the concentration changes are not too great. This assumption is relaxed in Kedem-Spiegler relationship (Section 1.2). Second, by considering the membrane as a "black box", the resulting analysis does not give any insight into the transport mechanism.

## 1.2. Irreversible Thermodynamics-Kedem Spiegler Relationship

Premises of the model. One critical assumption in the irreversible thermodynamics-phenomenological transport relationship is that the linear laws were assumed to apply over the whole thickness of the membrane. Spiegler and Kedem [23] resolved the problem by rewriting the original linear IT equations in differential form and then integrating them over the thickness of the membrane.

### Mathematical formulation of the model.

The equations in differential form for the solvent and solute flux, respectively are:

$$J_v = P_B \left( \frac{dp}{dx} - \sigma \frac{d\pi}{dx} \right) \quad (19)$$

$$N_A = P_A \frac{dC_{AM}}{dx} + (1 - \sigma) C_{AM} J_v \quad (20)$$

where  $p_A$  is the solute permeability,  $p_B$  is the water permeability, and  $x$  is the coordinate direction perpendicular to the membrane.

If  $p_A$ ,  $p_B$ , and  $\sigma$  are constant, Equation 19 can be integrated to give Equation 21, below, and Equation 20 can be integrated and combined with Equation 12 to give [21, 23] Equation 22 :

$$J_v = (p_B/\Delta x) (\Delta P - \sigma \Delta \pi) \quad (21)$$

$$\frac{1}{f} = \frac{1 - \sigma \exp[-(1-\sigma)(\Delta x/p_A) J_v]}{\sigma \{1 - \exp[-(1-\sigma)(\Delta x/p_A) J_v]\}} \quad (22)$$

The result is a three-parameter model described by Equations 21 and 22, similar to the previous phenomenological relationship but which should have coefficients that are independent of concentration and pressure. The three parameters in the Kedem-Spiegler relationship are  $p_B/\Delta x$ ,  $p_A/\Delta x$ , and  $\sigma$ .

This model has been used by various researchers to describe reverse osmosis transport [21, 22, 24, 25].

## 2. Mechanism Dependent Transport Models

In this section, models which specifically assume a membrane structure are described. First, models which consider the membrane to be nonporous are described and second, models which consider the membrane to be porous are described.

### 2. 1. Nonporous Transport Models

Several models have been derived that specifically assume that the membrane surface skin is nonporous have been derived. These models are usually based on a solution-diffusion mechanism. Modifications of this model, such as the solution-diffusion imperfection and the extended solution diffusion relationships are discussed briefly.

### 2. 1. 1. Solution-Diffusion Relationship

Premises of the model. The solution-diffusion (SD) model was originally applied to reverse osmosis by Merten and coworkers [26, 27]. The membrane surface layer is considered to be homogeneous and nonporous. Transport of both solvent and solute occurs by the molecules dissolving in the membrane phase and then diffusing through the membrane. The permeability of a species is equal to the product of the solubility and the diffusivity for that species. Theoretically, the solubility and the diffusivity of the solute can be determined for a membrane material by performing equilibrium sorption and unsteady state sorption/desorption studies, respectively. The water flux is proportional to the solvent chemical potential difference (usually expressed as the effective pressure difference across the membrane), and the solute flux is proportional to the solute chemical potential difference (usually given as the solute concentration difference across the membrane). The solute and solvent are assumed to be transported across the membrane independently.

#### Mathematical formulation of the model.

The solvent and solute fluxes, respectively are:

$$J_v = \frac{D_{BM} C_{BM} V_B}{RT \Delta x} (\Delta P - \Delta \pi)$$

$$N_A = \frac{D_{AM} K}{\Delta x} (C_{A2} - C_{A3})$$

Note that Equation 23 is identical to Equation 6, except that A has been replaced by more physically meaningful terms. The group of parameters in Equation 23 is abbreviated as the hydraulic permeability coefficient,  $\ell_p (= D_{BM} C_{BM} V_B / RT \Delta x)$ .  $D_{AM}$  and  $D_{BM}$  are the diffusivities of the solute and the solvent in the membrane, respectively;  $C_{BM}$



is the membrane water content;  $V_B$  is the partial molar volume of water; and  $K$  is the partition coefficient defined as follows:

$$K = \frac{\text{kg solute/m}^3 \text{ membrane}}{\text{kg solute/m}^3 \text{ solution}} \quad (25)$$

$K$  is a measure of the relative solute affinity to ( $K > 1.0$ ) or repulsion from ( $K < 1.0$ ) the membrane material.

As illustrated by Pusch [22], Equations 23 and 24 may be combined with Equation 12 and rearranged to give:

$$f' = 1 + \frac{D_{AM}K}{\Delta x} \left( \frac{1}{J_v} \right) \quad (26)$$

Equation 26 predicts a linear relationship between  $1/f'$  and  $1/J_v$ . Equations 23 and 26 can be fit to experimental data to generate the two parameters ( $D_{BM} C_{BM} V_B / RT \Delta x$ ) and ( $D_{AM}K / \Delta x$ ), both of which are treated as single quantities. In order to resolve either of these terms into component parts, it is necessary to have an independent measure of some of the terms (see, for example [28] on how to measure  $D_{AM}$ ,  $D_{BM}$ , and  $K$ , separately).

One restriction of the SD model is that the separation obtained at infinite flux is always equal to 1.0. However, this limit is not reached for many solutes. For this reason, the SD model is appropriate for solute-solvent membrane systems where the separation is close to 1.0. Notwithstanding this restriction the SD model has been applied to many different inorganic and organic solute systems with different types of membranes [22, 26-28]. The primary advantage of this model is that it is simple and as such has only two adjustable parameters.

### 2.1.2. Other Nonporous Transport Models

Several modifications to the original solution-

diffusion model have been proposed and two of these are discussed here briefly.

#### The solution-diffusion imperfection model.

This model was derived by Sherwood et al. [29]. The premise of this model is that during the membrane making process small defects in the membrane surface structure could result and these defects would lead to leakage of solution through the membrane. This mechanism would account for membranes that exhibited lower separation than the separation calculated based on solubility and diffusivity measurements. This model has been used successfully to describe the performance for a variety of solutes and membranes [15]. A mathematically similar model was proposed by Eriksson [30]. The main difference is that in Eriksson's work the two modes of transport were interpreted as diffusion in small pores and leakage through larger defects.

#### Extended Solution-Diffusion Relationship.

Both Burghoff et al. [24] and Jonsson [31] have pointed out that in the original solution-diffusion model, a pressure term in the solute chemical potential equation was neglected. Including this pressure term leads to a somewhat different form of the transport equations. The differences are primarily important for the situation when the solute partial molar volume is large and the solute-water separation is low. Burghoff et al. [24] found good agreement between the ESD model and the observed performance for different organic solutes with cellulose acetate membranes. The negative separation observed for phenol was attributed to a large pressure contribution to the flux of solute.

## 2.2. Porous Transport Models

In this section, transport models in which it is specifically assumed that the membrane

is porous are presented.

## 2.2. 1. Kimura-Sourirajan Analysis

Premises of the model. The Kimura-Sourirajan analysis (KSA) [5, 11] was developed based on the "preferential sorption-capillary flow" mechanism proposed earlier by Sourirajan [32]. According to the KSA relationship, the membrane surface is microporous and transport occurs only through the pores. The membrane has a preferential attraction for water and the resulting sorbed layer of almost pure water is forced through the membrane pores by pressure. Therefore solute separation and flux are determined both by physicochemical interaction between the solute-solvent-membrane system and by the number, size, and size distribution of pores.

### Mathematical formulation of the model.

The solvent flux is viscous in nature and therefore the driving force for solvent transport is given by the effective pressure as in Equation 6. The solute flux is diffusive in nature and is driven by the concentration gradient:

$$N_A = \frac{D_{AM}K}{\tau} (C_{A2} - C_{A3}) \quad (27)$$

Equations 6, 8, 12, and 27 together make up the Kimura-Sourirajan analysis. For dilute solutions these equations can be combined to give the following relationship between  $f'$  and  $J_v$ :

$$\frac{1}{f'} = 1 + \frac{D_{AM}K}{\tau} \left( \frac{1}{J_v} \right) \quad (28)$$

Note that this equation is functionally the same as for the SD model. The two parameters are  $A$  (from Equation 6 and  $(D_{AM}K/\tau)$ ). Even though Equation 28 is similar to Equation 26 for the solution-

diffusion model, the coefficients are interpreted differently. In the KSA model,  $D_{AM}$  is the diffusivity of the solute in the membrane pore rather than in the polymer material;  $K$  is the partition coefficient defined based on the amount of solute in the pores rather than in the membrane material; and  $\tau$  is the effective length of a pore, rather than the actual thickness of the membrane surface,  $\Delta x$ . As in the SD model, Equation 28 predicts that  $f'$  approaches 1.0 for infinite flux. This characteristic is not realistic for the many solutes that do not approach perfect separation at high solvent flux rates.

## 2.2. 2. Finely-Porous Model

Premises of the model. The finely-porous model developed by Merten [27], is based on a balance of applied and frictional forces, as first proposed by Spiegler [33], in a one-dimensional pore. A complete derivation of the model has been given by Jonsson and Boesen [15] and by Soltanieh and Gill [21].

### Mathematical formulation of the model.

The general form of this model relates the volume flux,  $J_v$ , and the separation,  $f'$ , as follows:

$$\frac{1}{f'} = \frac{1 - (1 - K_3/b) \exp[-(\tau/\epsilon D_{AB}) J_v]}{(1 - K_2/b) - (1 - K_3/b) \exp[-(\tau/\epsilon D_{AB}) J_v]} \quad (29)$$

The solvent flux is represented by Equation 6. The parameters in the relationship are the pure water permeability,  $A$ , the partition coefficients on the high and low pressure sides of the membrane,  $K_2$  and  $K_3$ , respectively, the friction parameter,  $b$ , the effective membrane thickness,  $\tau$ , and the fractional pore area of the membrane surface,  $\epsilon$ .

The partition coefficients,  $K_2$  and  $K_3$ , are defined in a manner similar to that given

earlier in Equation 25, with one difference. In this case, the concentration of solute in the membrane is interpreted as the concentration of solute in the membrane pore. The friction parameter,  $b$ , is defined [15] as:

$$b = (X_{AM} + X_{AB}) / X_{AB} \quad (30)$$

where  $X_{AB}$  represents friction between the solute and solvent and  $X_{AM}$  represents friction between the solute and membrane material. Therefore,  $b$  can be thought of as the ratio of the total friction of the solvent plus membrane upon the solute to the friction between solute and solvent. The frictional forces are inversely proportional to the diffusivity of solute within the membrane phase,  $D_{AM}$ , and the diffusivity of the solute in the free solvent,  $D_{AB}$ , so that Equation 30 can be rewritten as:

$$b = D_{AB} / D_{AM} \quad (31)$$

The friction parameter can be estimated based on the Faxen equation as discussed in references [15, 34-38].

The effective thickness of the membrane,  $\tau$ , is a product of the actual thickness of the membrane surface layer (membrane "skin" layer) multiplied by the tortuosity of the membrane pore. The tortuosity factor corrects the actual membrane skin thickness to an effective thickness that includes the non-linearity of the pore geometry.  $\epsilon$  is the fractional pore area of the membrane surface. For an asymmetric membrane, the value of  $\epsilon$  is much less than that calculated from the water content of the whole membrane.

The finely-porous model as represented by Equations 6 and 29, is a four parameter model; the four grouped parameters are  $A$ ,  $b/K_2$ ,  $K_3/K_2$ , and  $\tau/\epsilon$  which can be obtained

by fitting experimental reverse osmosis data to the model. The parameter,  $\tau/\epsilon$ , is a measure of the size and number of pores only, and should be a constant for a given membrane sample.

In principle,  $K_2$  and  $K_3$  may be different, but it is often assumed [15, 24, 28] that  $K_2 = K_3 = K$ . In order for this to be true,  $K$  should be independent of concentration, pressure, and membrane structure. When the above assumption is made, Equation 29 reduces to:

$$\frac{1}{f} = \frac{1 - (1 - K/b) \exp[-(\tau/\epsilon D_{AB}) J_v]}{(1 - K/b) \{1 - \exp[-(\tau/\epsilon D_{AB}) J_v]\}}$$

which is a three-parameter model. The three parameters are  $A$ ,  $b/K$ , and  $\tau/\epsilon$ .

Several authors [15, 24, 25, 27] have successfully used this model (usually in the three-parameter form) to describe the transport of various electrolyte and nonelectrolyte solutes through reverse osmosis membranes.

### 2. 2. 3. Modified Surface Force-Pore Flow Model

Premises of the model. Several authors have considered transport of solute and solvent in 2-dimensional right cylindrical pores. The advantage of using a model of this type is that the model should more accurately describe the transport in a porous membrane. The disadvantages are that the models are considerably more complex (usually involving advanced numerical techniques to solve the governing equations) and the models are still considerable simplifications of the real situation. Nonetheless these models can be useful and therefore a description is given here.

The original work in this area was concerned with the transport in electro dialysis type membranes so that electrical potential driving

and therefore can be dropped; the term becomes important when there is strong attraction between the solute and membrane. If the last term is dropped and if  $(1 - \exp(-\Phi(\rho)))$  is approximately 1, then the solution of equation 48 is the Poiseuille equation with pressure replaced by the effective pressure  $(\Delta P - \Delta \pi)$ ; in other words apparabolic velocity profile.

The water flux and the solute flux can be calculated as:

$$N_B = \frac{2 D_{AB}}{\tau/\epsilon} C \int_0^1 \alpha(\rho) \rho \, d\rho \quad (44)$$

$$N_A = \frac{2 D_{AB}}{\tau/\epsilon} \int_0^{1-\lambda} \alpha(\rho) \rho (C_{A2} + \frac{C_{A2} - C_{A3}}{e^{\Phi(\rho)} - 1}) \frac{e^{-\Phi(\rho)}}{b(\rho)} \, d\rho \quad (45)$$

Then Equation 11 can be used to calculate the permeate concentration,  $C_{A3}$ .

The solution procedure is iterative and can be summarized as follows:

1. Assume that the parameters in the model and the operating conditions are known or determined by an optimization code.
2. Guess the permeate concentration,  $C_{A3}$ .
3. Solve Equation 41 subject to Equations 42 and 43 for the velocity profile  $\alpha(\rho)$  by a numerical technique (e.g. "orthogonal collocation").
4. Calculate the water and solute flux from Equation 44 and 45 and hence the permeate concentration  $C_{A3}$  from Equation 11 (using numerical integration).
5. Check  $C_{A3}$  with guessed value and iterate if necessary.

Note that the only adjustable parameters in the model are the average pore size,  $R_W$ , a parameter depended on the thickness of the membrane and number of pores  $\tau/\epsilon$ , and the potential parameters  $\theta_1$  and  $\theta_2$ .

### 3. Summary and Comparison of Transport Models

It is interesting to note that several of the models presented or discussed above have similar mathematical forms; particularly in terms of the predicted relationship between flux and separation. For instance, both the solution-diffusion model and the Kimura-Sourirajan analysis, and the irreversible thermodynamics-Kedem Spiegler model and the finely-porous model are mathematically identical. Some of these similarities have been discussed previously [15, 21]. Yet each of these models is based on substantially different assumptions. What this tells us is that simple agreement between experimental data and a model is not proof that the model is correct. In this light, care must be exercised in interpreting model parameters calculated from these models. For a membrane maker, using a porous model will give information about the porous nature of the membrane, and using a solution diffusion model will give information about the diffusion and solubility coefficients in the membrane. Until the nature of the membrane structure is resolved the decision of which model to use, is, in part, a matter of personal choice.

For the person who is only interested in the application of a membrane, using the following equation (originally suggested, in this form, by Soltanieh and Gill [21]) is a reasonable compromise:

$$\frac{1}{1-f} = E_1 - E_2 \exp(-E_3 J_v) \quad (46)$$

This equation is mathematically equivalent to the Kedem-Spiegler and the finely-porous models. The coefficients,  $E_1$ ,  $E_2$ , and  $E_3$  can then be treated as empirical parameters that must be determined for each new solute and membrane system.

## SYSTEM DESIGN

The transport equations discussed above are useful for relating the membrane performance (flux and separation) in terms of the operating variables and some transport parameters. However, these models all assume that the amount of permeate collected is small compared to the feed rate (~zero recovery). In a membrane module or membrane plant the permeate is a significant fraction of the feed rate (finite recovery). The transport equations are valid at any point within the membrane module, but to describe the overall module (or system) behaviour it is necessary to integrate this solution over the length of the membrane system. In this section, two of the methods of handling this problem are reviewed.

In general the problem is handled by first assuming a model to describe the membrane mass transfer, and then the model is integrated over the length of the membrane system. This ultimately relates the choice of membrane module, number and arrangement of modules, and the operating conditions to the system performance in terms of permeate recovery and separation.

### 1. Membrane Module Configuration

Several different technologies have been developed to put a large membrane area into a relatively small volume. The most popular of these designs are: spiral wound, hollow fibre, and tubular. The relative merits of each of these designs is dependent on the particular application. A review of the merits of the different designs is presented elsewhere [47].

### 2. Method of Saltonstall and Lawrence

In this method [48] several simplifying assumptions are made. The membrane is assumed to have a constant separation in-

dependent of operating conditions ( $f = \text{constant}$ ), the mixing on the high pressure side of the membrane is sufficiently high that  $k \rightarrow \infty$  (no concentration polarization), there is no pressure drop in the feed channel, and the physical properties of the solution are constant (constant density and viscosity).

The equations are summarized as follows:

$$C_{A1}^f = C_{A1}^o (1 - Y)^{-f}$$
$$\bar{C}_{A3} = C_{A1}^o \frac{1 - (1 - Y)^{1-f}}{Y}$$

where  $C_{A1}^f$  is the final concentrate concentration,  $C_{A1}^o$  is the inlet feed concentration,  $f$  is the constant separation, and  $Y$  is the recovery defined as:

$$Y = Q_3 / Q_1^o$$

where  $Q_1^o$ ,  $Q_1^f$ , and  $Q_3$  are volumetric flow rates of the feed, concentrate and permeate, respectively. By material balance:

$$Q_1^o + Q_1^f + Q_3 \quad (50)$$

These equations give simple relationships between the separation and recovery and the operating conditions for a system. The approach breaks down if the separation varies too much through out the system under consideration.

### 3. Method of Sourirajan and Ohya

In the method of Sourirajan and Ohya [49] again several simplifying assumptions are made, but the approach is more general than the one above. The required assumptions are: the membrane mass transfer is described by the KSA model, molar density is constant, osmotic pressure is linear with concentration, solute flux is small compared to solvent flux, transport parameters are constant, and no longitu-

dinal diffusion of the solute in the feed flow direction. Although these assumptions are lengthy, the model is much more general than assuming constant separation as by the above method. Although an analytical solution is reached, the solution requires the solution of several simultaneous equations including a double integral. The design equations are given on p. 72 of reference 49.

## CONCLUSIONS

The main conclusions of this paper are as follows. There have been many models proposed to describe and to predict the performance of reverse osmosis type membranes. These models are built on different assumptions and have different degrees of complexity, but all of them are successful at describing simple performance data. It is necessary to integrate the transport equations over the length of the system for large RO systems with finite permeate recovery. Two methods of doing this integration are presented. In part two of this paper, the predicted behaviour of transport models will be demonstrated and the effect of operating conditions on membrane performance will be presented.

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## APPENDIX I. NOMENCLATURE

a	Empirical coefficient defined by Equation 9.
A	Pure solvent permeability coefficient, $\text{kmol/m}^2 \text{ s kPa}$ .
b	Friction parameter defined by Equation 30.
b'	Empirical coefficient defined by Equation 9.

C	Molar density, $\text{kmol/m}^3$ .
$C_{Ai}$	Molar concentration of species A at location i, $\text{kmol/m}^3$ .
$C_i$	Molar concentration of species i in solution, $\text{kmol/m}^3$ .
$C_{ij}$	Molar concentration of component i in phase j, $\text{kmol/m}^3$ .
$(C_{ij})_{\ln}$	Logarithmic mean concentration of i in phase j, $\text{kmol/m}^3$ .
$D_{ij}$	Diffusivity of component i in component j, $\text{m}^2/\text{s}$ .
$(D_{iM}K/\tau)_i$	Solute transport parameter for solute i, m/s.
$E_1, E_2, E_3$	Generalized transport parameters in Equation 46.
$F_i$	Generalized thermodynamic force defined by Equation (13).
f	Separation.
f'	Separation based on the boundary layer concentration.
$J_i$	Generalized thermodynamic flux defined by Equation 13.
$J_v$	Solvent volume flux, $\text{m}^3/\text{m}^2 \text{ s}$ .
K	Solute partition coefficient.
$K_i$	Solute partition coefficient at location i.
k	Mass transfer coefficient, m/s.
$L_{ij}$	Generalized thermodynamic phenomenological coefficients defined by Equation 13.
$\rho_p$	Hydraulic permeability coefficient, m/s kPa.
$\rho_\pi$	Osmotic permeability coefficient, m/s kPa.
$m_{ij}$	Molality of species i at location j, $\text{kmol/m}^3$ .
$N_i$	Molar flux of component i, $\text{kmol/m}^2 \text{ s}$ .
$N_{Sc}$	Schmidt number.
$N_{Sh}$	Sherwood number.
$N_{Re}$	Reynolds number.
P	Hydrostatic pressure, kPa.
$\Delta P$	Pressure difference across the membrane, kPa.
$\Delta P$	Dimensionless pressure difference

	<b>defined by Equation 36.</b>
PA	Solute permeability coefficient, $m^2/s$ .
PB	Water permeability coefficient, $m^2/s$ kPa.
R	Gas constant, kJ/kmol K.
R <sub>W</sub>	Radius of pore, m.
r	Radial position in a pore m.
T	Temperature, K.
u <sub>B</sub>	Velocity of solvent in a pore, m/s.
V <sub>i</sub>	Partial molar volume of component i, $m^3/kmol$ .
	Mole fraction of solute A at location i.
X <sub>B</sub>	Mole fraction of solvent.
x	Coordinate direction perpendicular to the membrane, m.
Δx	Membrane thickness, m.

### Greek Symbols

α	Dimensionless solvent velocity in a pore as defined by Equation 34.
β <sub>1</sub>	Dimensionless ratio defined by Equation 35.
ε	Fractional pore area.
η	Solution viscosity, kPa s.
θ <sub>1</sub>	Potential parameter in Equation 38, m.
θ <sub>2</sub>	Potential parameter in Equation 38, dimensionless.
λ	Ratio of solute radius to pore radius.
μ <sub>i</sub>	Chemical potential of component i, kJ/kmol.
Δμ <sub>i</sub>	Chemical potential difference across the membrane for component i, kJ/kmol.
π <sub>i</sub>	Osmotic pressure of solution at location i, kPa.
Δπ	Osmotic pressure difference across the membrane, kPa.
Δπ	Dimensionless osmotic pressure difference defined by Equation 37.

ρ	Dimensionless radial position in a pore as defined by Equation 33.
σ	Reflection coefficient.
τ	Effective thickness of a membrane, m.
Φ	Dimensionless potential function of force exerted on a solute molecule by a pore wall.
X <sub>ij</sub>	Friction coefficient between components i and j, kJ s/kmol m <sup>2</sup> .
ω	Transport parameter defined by Equation 18, kmol/m <sup>2</sup> s kPa.

### Subscripts

A	Solute
B	Solvent
M	Membrane
ref	Reference
T	Total solution
W	Wall
1	Feed solution
2	Boundary layer solution
3	Permeate solution

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