OVERVIEW OF REVERSE OSMOSIS FOR CHEMICAL ENGINEERS
PART 2: APPLICATIONS OF TRANSPORT MODELS

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Abstract   This second part of the overview of reverse osmosis investigates the ability of membrane transport models, presented in Part 1, to descrebe and/or predict membrane performance under different operating conditions. The problem of using the transport models to describe mixed solute systems is also discussed. 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   مقالهٔ حاضر قسمت دوّم از سری بررسیهای پدیده های انتقال درفرآیند اسمز معکوس می باشد که به بررسی توانائی مدلهای انتقال ماده از درون غشاء جهت توصیف و یا تخمین عملکرد غشاء تحت شرایط آزمایشی مختلف می پردازد (مدلهای انتقال از درون غشاء در مقالهٔ قسمت اول آمده اند). با استفاده از مدل جهت توصیف سیستم های چند جزئی نیز بحث شده است. در این مقاله تأکید بر آنست که خلاصه ای ساده، عملی، و جامع از اطلاعاتی که یک مهندس شیمی جهت استفاده از غشاء های اسمز معکوس بدان نیاز دارد دراختیار خواننده قرار گیرد. توانائی مدل پیشنهادی توسط مؤلفین مقاله نیز در این مقاله بطور مختصر بحث شده است.

INTRODUCTION

In a previous paper [1] an overview of several transport models that are commonly used to describe membrane transport was presented. The study of transport in membranes is interesting enough in itself. However,the real power of a transport model comes when it is used to describe and to predict the behavior of real membranes under various experimental condittons. Without the capability of prediction, the interest in transport modeling ends at the academic level. This paper addresses the application of transport models for describing and predicting membrane behavior.

The authors'personal preferences for choosing a transport model are as follows. If the solute is highly rejected by the membrane and no unusual behavior is expected, then the Kimura-Sourirajan Analysis is quite sufficient. The advantages of this model are that it is simple and that many correlations for predicting

the transport parameters have been published [2-4]. If the solute is not highly rejected then finely-porous model is preferred. the advantage of this model is that it can well describe the relationship between performance and operating conditions and only one extra transport parameter is required. An equivalent phenomenological approach uses Equation (46), from refernce 1, which is mathematically similar to several different models, including the finely porous model. Finally, if unusual behavior is expected, such as occurs when the solute and membrane have a strong affinity for each other, then modified surface force-pore flow (MD-SF-PF) model is preferred.

The application of transport modelling can be broken down into several cases. The first, and easiest case is to predict the performance of a membrane for one solute but under a variety of different operating conditions. The second and considerably more difficult case is to predict for different solutes. The third and most difficult

case is the prediction for mixed solute systems. Finally, other complications that can arise are considered at the end of this paper.

THE EFFECT OF OPERATING CONDITIONS

Based on sales literature and on publications from membrane manufacturers, one might perceive that each membrane has a characteristic performance (that is, flux and separation) for each solute, independent of the operating conditions. This assumption is convenient in that tables of flux and separation, as a function of solute, for a particular membrane are easy to construct. However, this information is misleading. The actual performance of the membrane can be a strong function of the operating conditions, and the person designing a membrane system must take this into consideration. The effect of the major operating variables, concentration, pressure, feed flow rate, temperature, and pH are described in turn. What we hope is that the transport model will do an accurate job of predicting the membrane performance as a function of operating conditions to aid the engineer in the design process.

The Effect of Concentration

Feed concentration can have marked effect on membrane performance and the primary reason for this effect is the increase in osmotic pressure with increasing concentration. As concentration increases flux tends to decrease. Interestingly, as concentration is increased separation first increases and then decreases (see Figure 1). The initial increase in separation is due to the rapid decrease in flux which actually lowers the concentration polarization. Further increases in concentration lowers the effective pressure driving force and, as is shown in the next section, the separation decreases.

The effect of feed concentration, as predicted by the MD-SF-PF model [1,6], on aromatic polyamide FT30 commercial membranes has been discussed elsewhere[7]. Figure2 illustrates
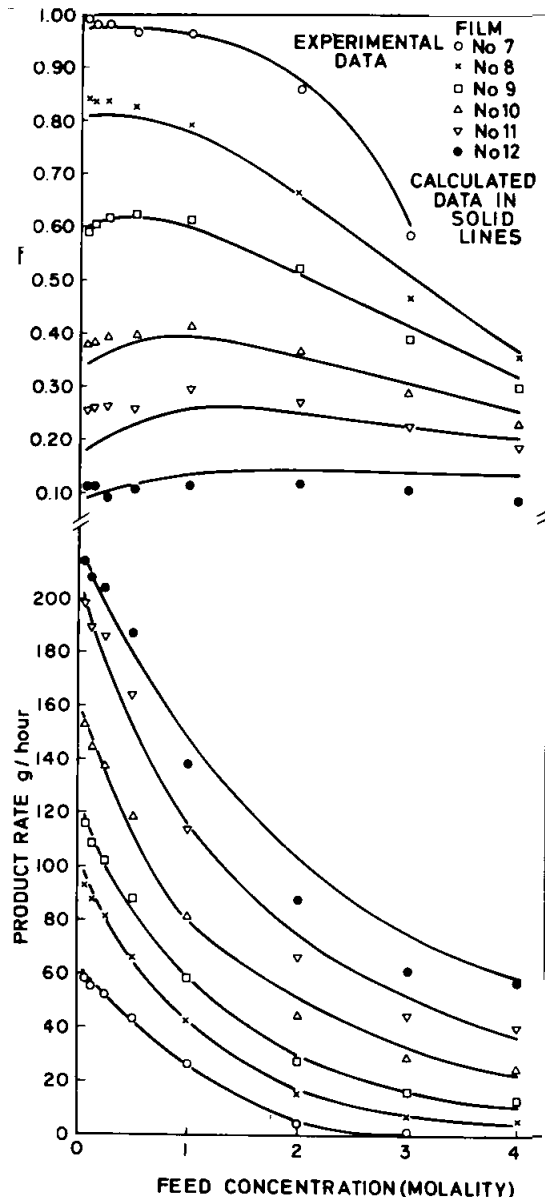

Figure 1. Comparison of the experimental and calculated (using the Kimura Sourirajan analysis) reverse osmosis performance for NaCl-Water system for a variety of cellulose acetate membranes with different porosities (with permission from reference [5]).

the effect on the performance of a SW30-HR (Sea Water-High Rejection) type of these membranes for dilute (2000-ppm) NaCl aqueous solutions at 1500 kPa and 25°C. The parameters of the model were estimated at 2000 ppm NaCl concentration.
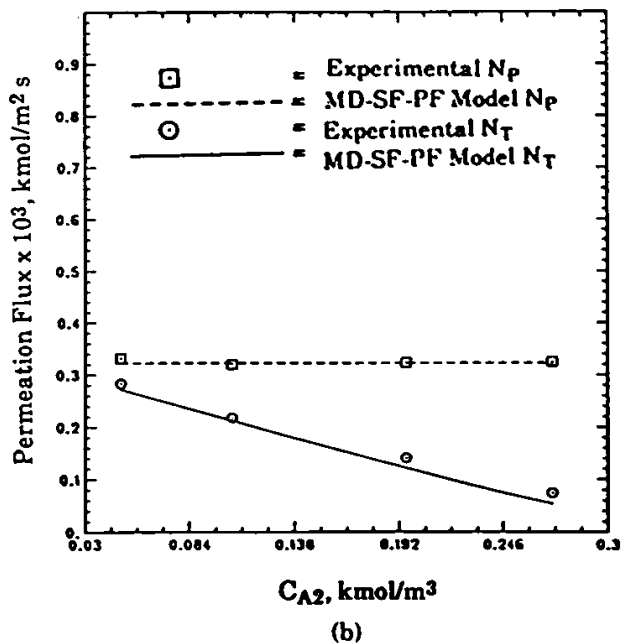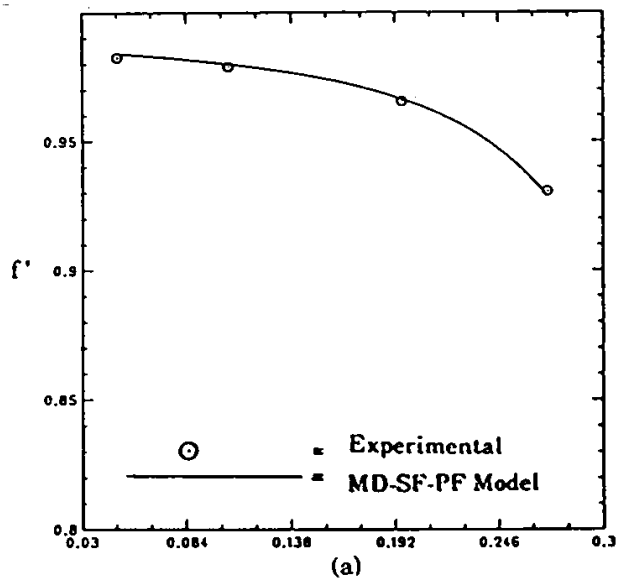
Figure 2. The effect of feed concentration on the performance of a FT30 (SW30-HR type) membrane for dilute NaCl-water solutions at 1500 kPa and 25°C (with permi- ssion from reference [7]).

The Effect of Operating Pressure

The primary effect of increasing the operating pressure is to increase the driving force for solvent (See Equation (6) of reference1) while only marginally affecting the driving force for solute. With perfect mixing on the high pressure side of the membrane $(k \rightarrow \infty)$ the separation increases rapidly with operating pressure and then levels off at a constant value (see Figure 3). If the mass transfer coefficient is finite then a small decrease in separation may be observed after the initial increase. Increasing operating pressure can also compact the membrane. This effect can often be represented by a linear decrease with pressure [8].

The Effect of Feed Flow Rate

The primary effect of feed flow rate is to change the mixing in the test system. Therefore the only influence of feed rate should be on the mass transfer coefficient, k. Of course, in a large membrane system feed rate also affects the pressure drop across the feed side channel, but that is not of concern in this paper. The effect of changing the feed rate and hence the mass transfer coefficient is illustrated in Figure 4. Equation (9) or (10) of reference 1 can be used to describe the effect of feed rate on mass transfer coefficient.

The Effect of Temperature

The most important effect of temperature is the increase in flux associated with increasing temperature. This increase in flux can be well described by an Arrhenius temperture dependence for the pure water permeability coefficient in Equation (6) of reference 1 as:

$$A = A_o exp(-E_o/RT) \qquad (1)$$

were E_o is the apparent activation energy associated with the solvent transport process. The activation energy for most membranes is above 17000 kJ/kmol (which is the value expected based on the change in the viscosity of free water). Figure 5 represents the Arrhenius relationship for four thin-film composite membranes (FT-30) as the pure water permeability at zero pressure (i. e , in the absence of compaction) versus 1/T [8].

Modeling the effect of temperature has been examined by several authors [9, 11,12]. Usually an Arrhenius equation (as above) is applied to each of the parameters in the transport model.
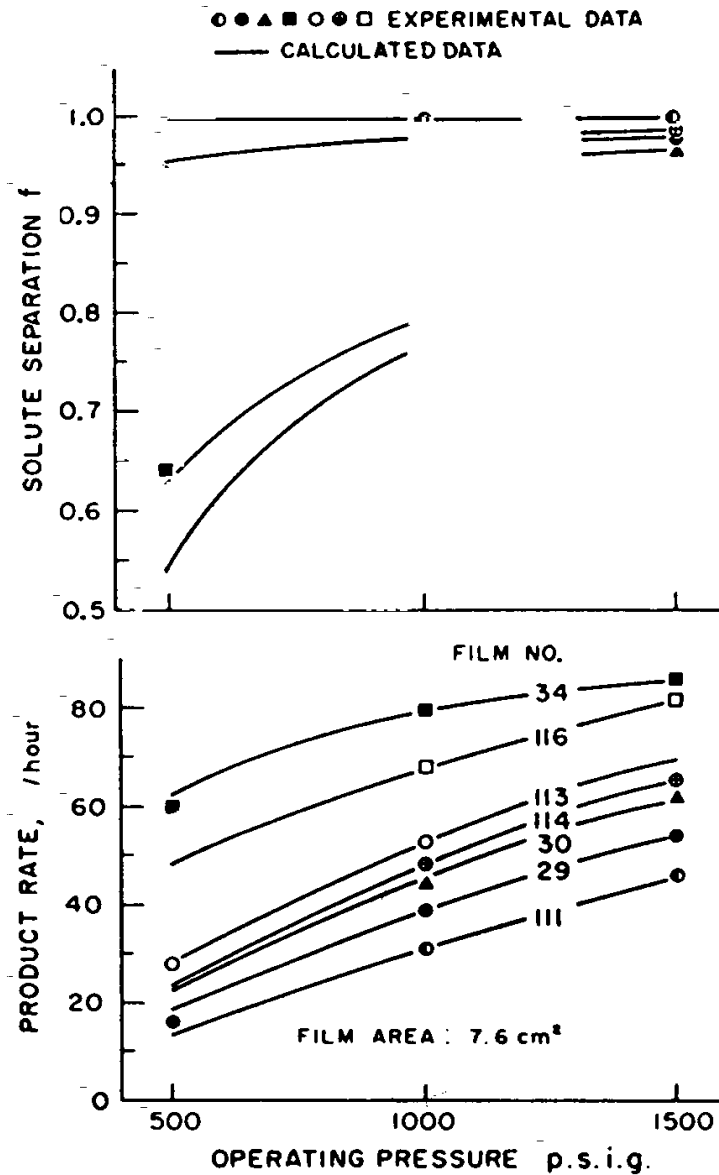
Figure 3. The effect of operating pressure on reverse osmosis performance for 0.5 M sucrose- water solutions for several different cellulose acetate membranes. The lines are calculated using the Kimura- Sourirajan analysis (with permission from reference [10]).

Connell and Dickson [12] have demonstrated how the finely—porous model can be modified to describe the temperature dependency for toluene–water–cellulose acetate system. Finally, Mehdizadeh and Dickson [8] studied the temperature effects on four thin—film composite, aromatic polyamide FT30 commercial membranes over the wide ranges of 5–60°C and 350–7000 kPa for dilute (2000 ppm) NaCl–water solutions, and found that separation is independent of temperature at higher pressures, but, for lower pressures, passes through a minimum and increases again with increasing temperature (see for example Figure 6); the permeation flux increased significantly with temperature [8].

The Effect of pH

In many cases the effect of pH can be ignored from a transport modeling point of view. The two exceptional cases are as follows. If the pH is
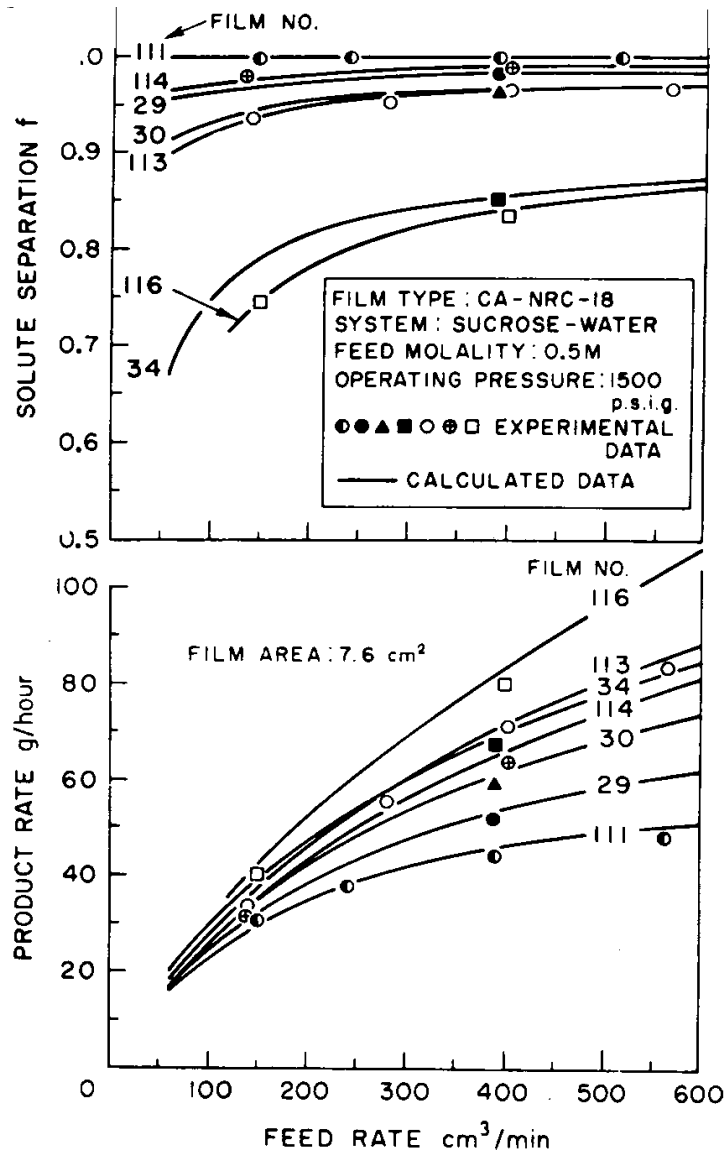
Figure 4. The effect of feed flow rate on the reverse osmosis performance for several different cellulose acetate membranes The lines are calculated using the kimura- Sourirajan analysis (with permission from reference [10]).

too high or low for the membrane, then the performance will decrease irreversibly and the membrane should be replaced. The manufacturers usually supply limits on the pH for their membranes.

The other exceptional case is when the solute becomes ionized as a result of a change in pH. One dramatic example of this is the case of solute phenol with cellulose acetate membranes [13]. At lower pH the phenol is completely undissociated and the separation is about zero (Figure 7). As the pH is increased, phenol dissociates and the separation increases until at pH>12 the phenol is totally dissociated and the separation becomes independent of pH again. The shape of the separation curve follows the degree of dissociation curve. These results indicate that the neutral phenol is approximately not separated at all and the dissociated phenol is highly separated. When the solute is partially
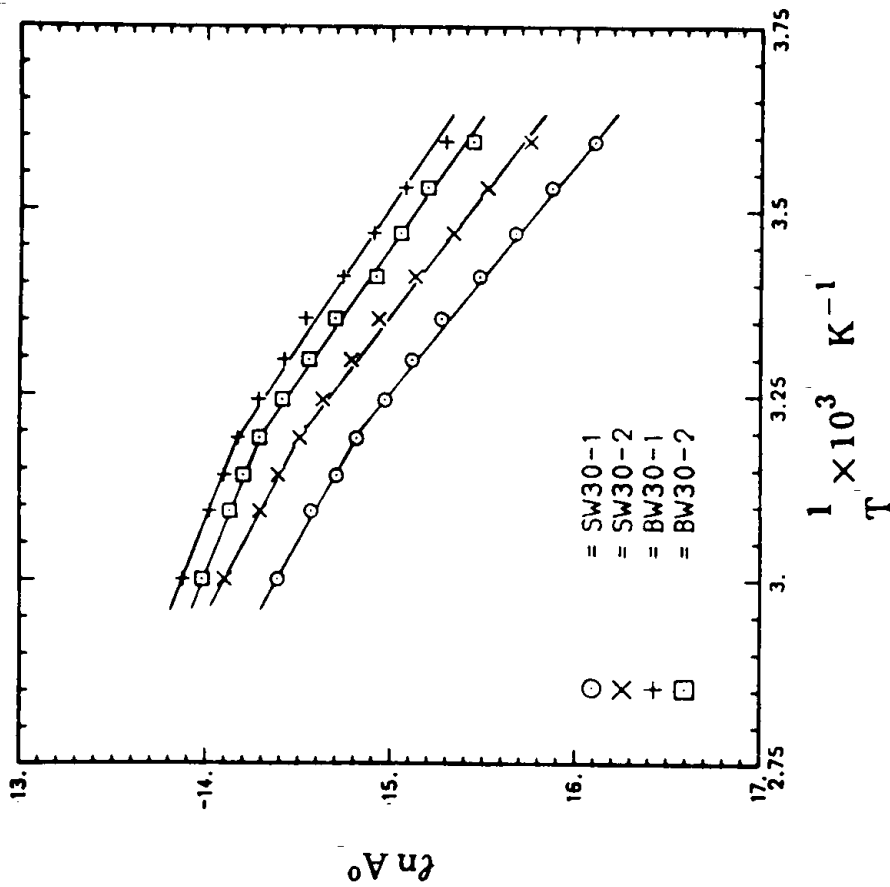
Figure 5. Arrhenius relationship between the pure water permeability coefficient extrapolated to zero pressure, A0, and temperature for four aromatic polyamide thin-film composite FT30 membranes (with permission from reference [8]).
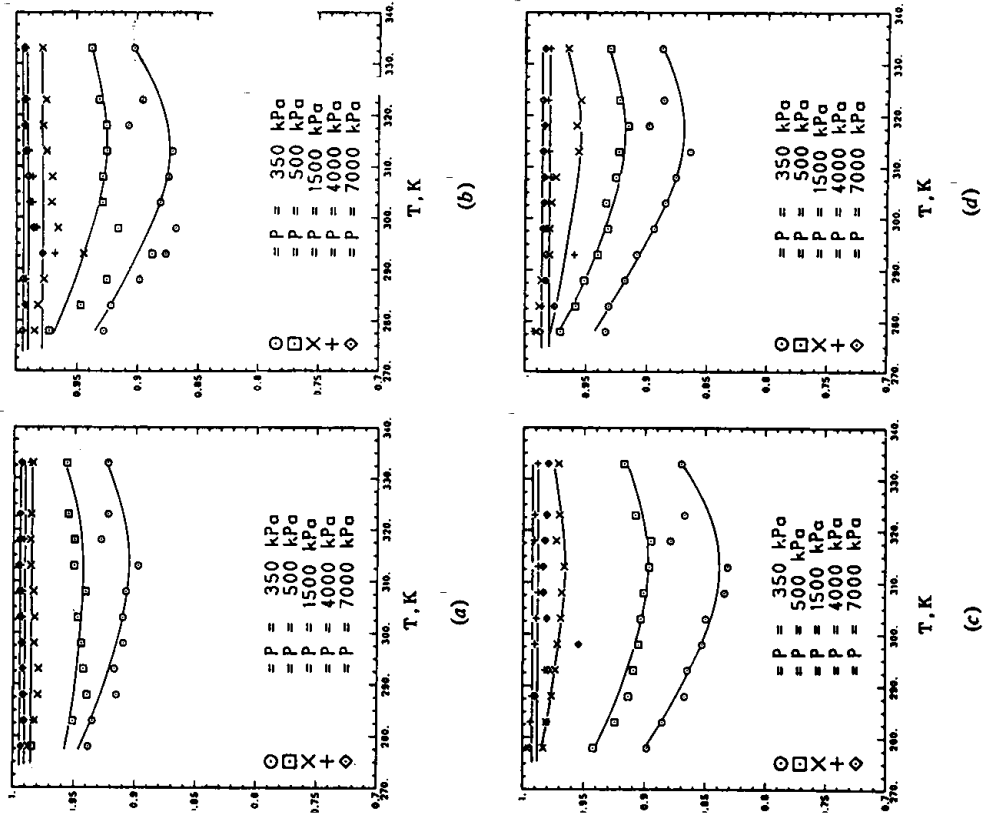
Figure 6. Separation as a function of temperature for four aromatic polyamide thin-film composite FT30 membrane (with permission from reference [8]).
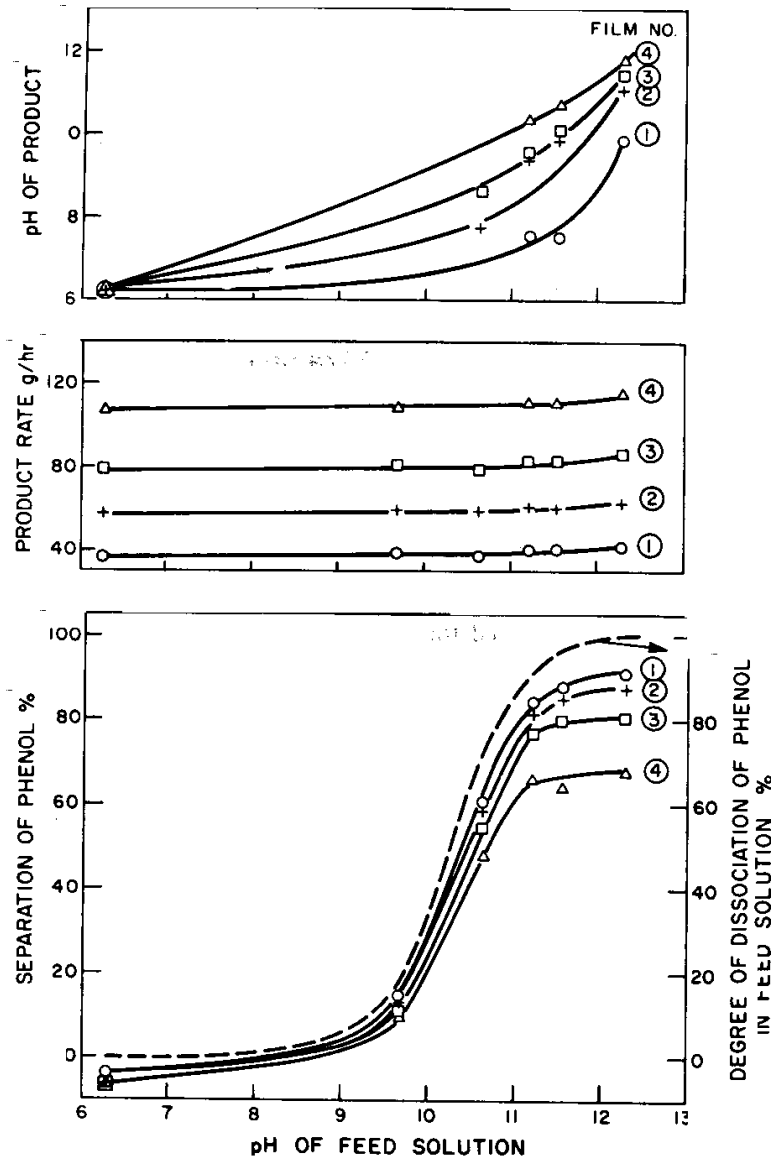
Figure 7. Effect of pH of feed solution and degree of dissociation of phenol on the reverse osmosis performance for several different cellulose acetate membranes (with permission from reference [13]).

dissociated then intermediate separation is obtained. Therefore, separation can be dramatically affected by changing the pH for ionizable solutes.

Predicting the Effect of Operating conditions

Predicting the effect of operating conditions on the membrane performance for the same solute requires the use of one of the transport models described before[1]. For example, applying the

Kimura–Sourirajan analysis to limited data, the transport parameters, A $D_{AM}K/t$, and k can be determined. These parameters are then used to predict the effect of operating conditions on membrane performance. This prediction is illustrated for the effect of feed concentration, operating pressure, and feed flow rate in Figures 1,3, and 4. The agreement between the theoretical curves and experimental data is good. Predicting the effect of operating conditions by the MD-SF-PF model has been shown in

reference 7 and, partly, in Figure 2. Equation (1) does a good job of describing the dependence of flux on temperature, and the separation is approximately independent of temperature. The effect of pH is more difficult to predict for ionizable solutes (such as phenol shown in Figure 7) because the system is essentially a mixed solute system. Methods of handling mixed solute systems are discussed below.

PREDICTION FOR DIFFERENT SOLUTES

The real power of a transport model is the ability to predict performance for solutes that have not yet been tested. This capability is of obvious advantage to the removal of organic solutes from water since there are many more organic solutes than can be reasonably tested for each membrane that is commercially available.

How can we do this prediction? It is apparent that the flux and separation should be a function of both the physical and the chemical nature of the solute— solvent membrane system. Therefore, one method of prediction is to examine the relationship between the transport model parameters and the physicochemical nature of the solute for a fixed solvent-membrane system. In principle this technique can be applied to any of the transport models reviewed before[1]. However, the vast majority of this type of correlation work has been done using the Kimura– Sourivajan Analysis (KSA) and therefore this is the method that is emphasized in this section.

Prediction With the Kimura- Sourirajan Analysis

Recall that the three parameters required for the KSA model are: the pure water permeability coefficient, A, the solute transport parameter, $D_{AM}K/\tau$, and the mass transfer coefficient, k. For a given membrane, the pure water permeability coefficient, A, is independent of solute and is reasonably independent of pressure. The mass transfer coefficient, as described above, is dependent on flow regime in the test equipment and can be well characterized by an

equation of the form of Equation (9) or (10) of reference 1. Therefore, the prediction problem simplifies to predicting, $D_{AM}K/\tau$ for various solutes. That $D_{AM}K/\tau$ is reasonably independent of concentration, feed rate, and almost independent of pressure is illustratid in Figure 8-10.

Prediction of the solute Transport Parameter

For a given membrane material it is reasonable to expect that the grouped transport parameter, $D_{AM}K/\tau$, is a function of physicochemical nature of the solute. Based on this premise, sourirajan and coworkers [3,4] have correlated a large amount of experimental data for many different inorganic and organic solutes for several different membrane types. The bulk of this work has been summarized in a recent book [4] and therefore only an outline of the results is given here.

For inorganic solutes that are completely dissociated, the solute transport parameter is related to the free energy required to move the solute cation and anion from bulk solution to the membrane solution interface. Using an extended form of the Born equation [15,16] to describe this free energy change. the following semiempirical equation was derived and used to correlate data:

$$\ln (D_{AM}K/\tau)_{MX} = \ln C^*_{NaCl}$$
$$+ n_c I_{M^+} + n_a I_{X^-} \quad (2)$$

where, $I_{M^+} = (-\Delta\Delta G/RT)$ for the cation M^+ (3)

$I_{X^-} = (-\Delta\Delta G/RT)$ for the anion X^- (4)

n_c and n_a are the number of cations and anions, respectively, in the salt formula (ie. for NaCl, $n_c = 1$ and $n_a = 1$; for $MgCl_2$, $n_c = 1$ and $n_a = 2$; and for $MgSo_4$ $n_c = 1$ and $n_a = 1$) and ln C^* NaCl represents the pore size of the membrane determined based on a reference salt NaCl.

Some examples of the single ion quantities, I_{M^+} and I_{X^-}, are presented in Table 1 for cellulose acetate membranes, and in Table 2 for some other membrane materials. Interpreting and

Figure 8. The effect of feed concentration on the solute transport parameter for several different cellulose acetate membranes (with permission from reference [2]).

correlating the data to give single ion quantities make the prediction for different salts a simple procedure. Simply add the single ion quantities for the new salt and use Equation (2) to calculate $D_{AM}K/\tau$. To apply this analysis to other membrane materials it is necessary to consult the original reference [4] to examine how to correlate data for different salts in terms of Equation(2).

For organic solutes that are undissociated a similar analysis is used to predict $D_{AM}K/\tau$ in terms of the physicochemical nature of the solute. According to the analysis of Sourirajan and coworkers [4,17] the physicochemical nature of the solute can be divided into polar effects, steric effects, and nonpolar (dispersive) effects. As such, the following semiempirical relationship is used:
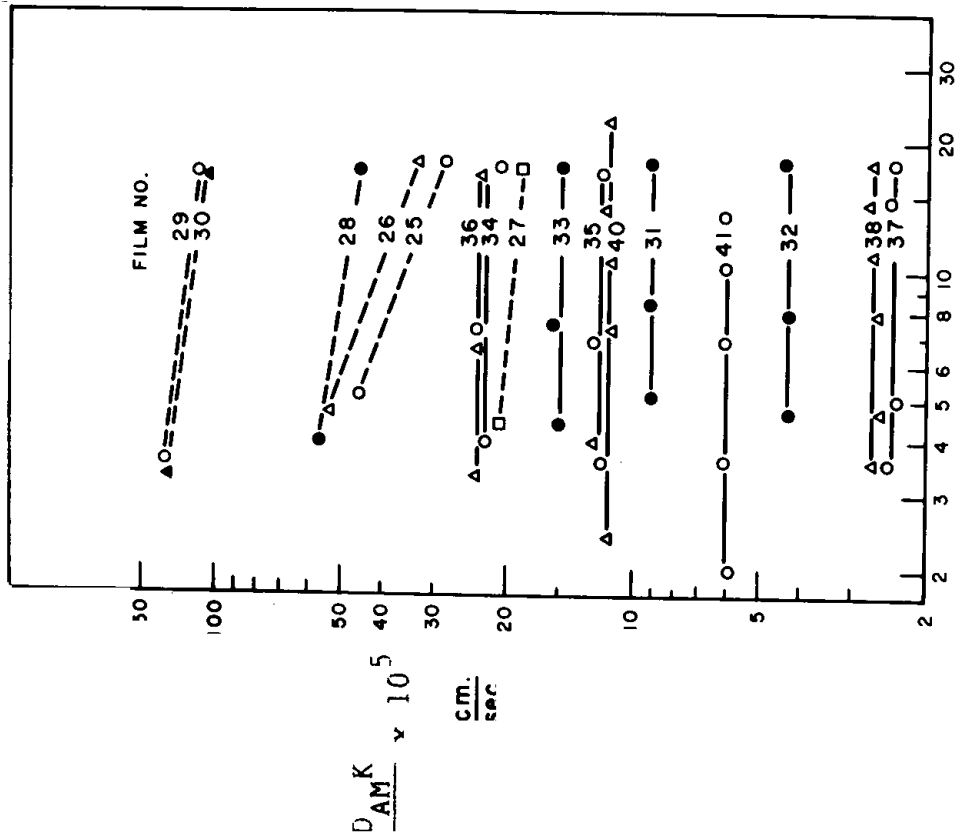
Figure 10. *The effect of operating pressure on the solute transport parameter for NaCl-water system for several different cellulose acetate membranes (with permission from reference [2]).*

FILM NO.

29
30

28
26
25

36
34
27

33

35
40

31

41

32

38
37

$\dfrac{D_{AM}K}{\text{---}} \times 10^5 \ \dfrac{cm.}{sec.}$

OPERATING PRESSURE - atm.

FILM TYPE : CA - NRC - 18
SYSTEM : UREA - WATER
FEED MOLALITY : 0.5M O △ □ ▽
2.0 M ● ▲ ■ ▼
OPERATING PRESSURE : 1500 p.s.i.g.

FILM NO.

99

104

102

101

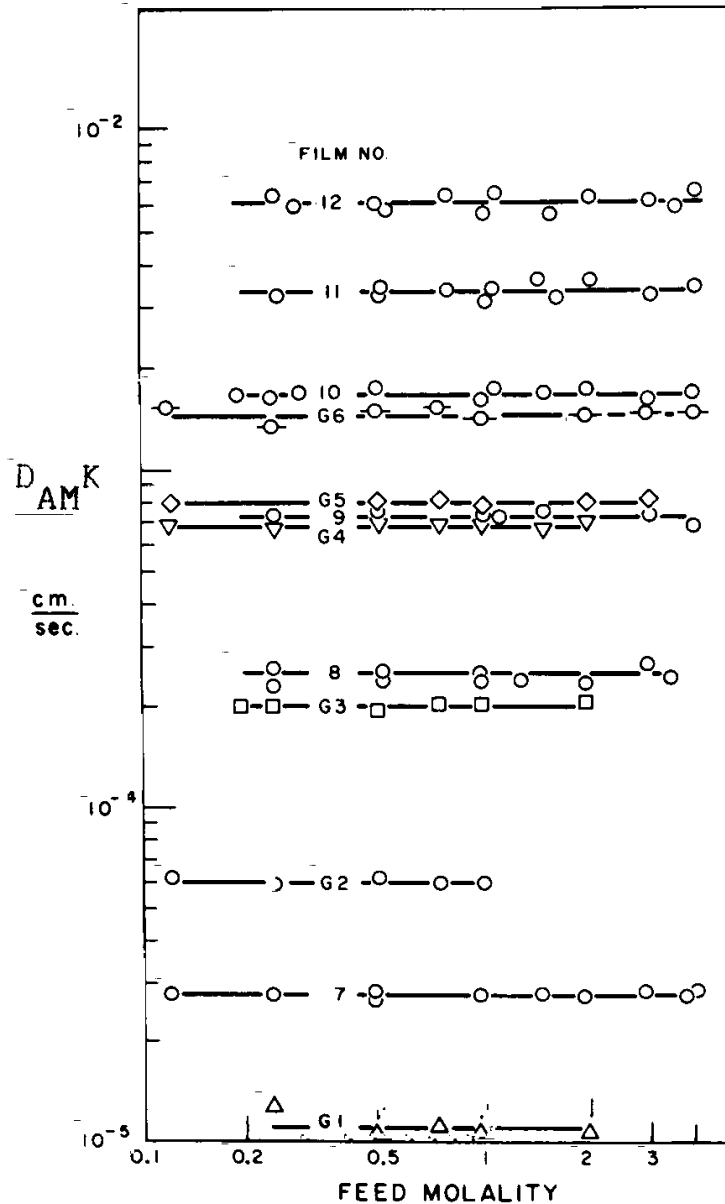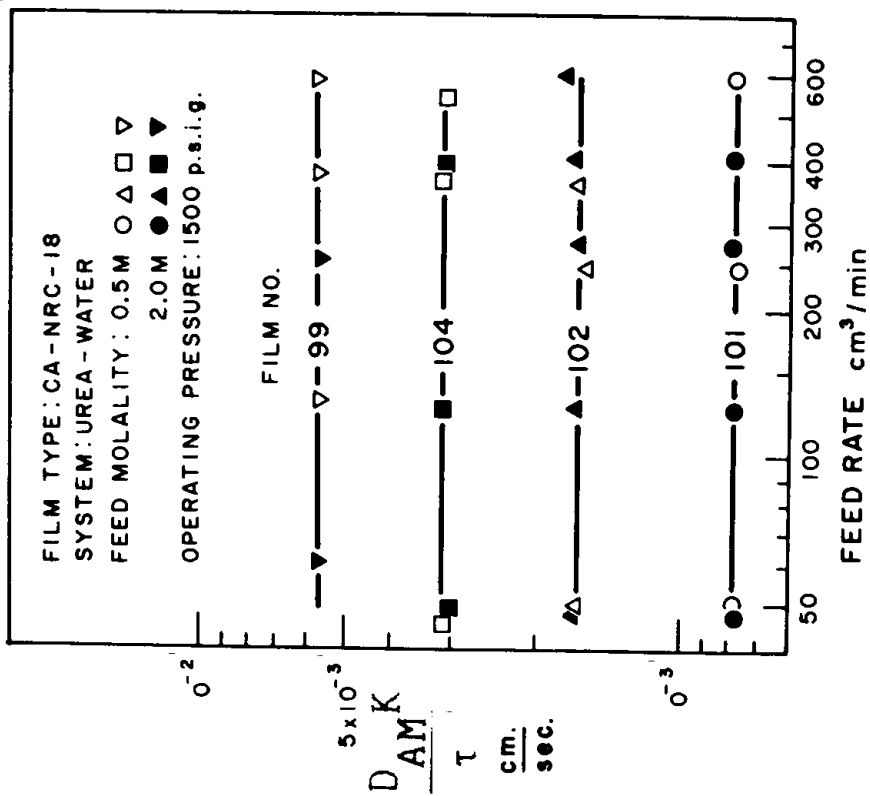$\dfrac{D_{AM}K}{\tau} \ \dfrac{cm.}{sec.}$

5×10⁻³

FEED RATE cm³/min

Figure 9. *The effect of feed flow rate on the solute transport parameter for several different cellulose acetate membranes (with permission from reference[14]).*

Table 1. Free Energy Parameter $(-\Delta\Delta G/RT)i$ *Data for Some Inorganic Ions and Ion-Pairs. Values are applicable for aqueous solutions and cellulose acetate membranes.* *

Inorganic Cations		Inorganic Anions		Inoranic Ion-pairs	
Species	$(-\Delta\Delta G/RT)i$	Species	$(-\Delta\Delta G/RT)i$	Species	$(-\Delta\Delta G/RT)i$
H^+	6.34	OH^-	-6.18	$MgSO4$	3.45
Li^+	5.77	F^-	-4.91	$CoSO4$	3.41
Na^+	5.79	Cl^-	-4.42	$ZnSO4$	2.46
K^+	5.91	Br^-	-4.25	$MnSO4$	2.48
Rb^+	5.86	I^-	-3.98	$CuSO4$	2.85
Cs^+	5.72	IO_3^-	-5.69	$CdSO4$	3.04
NH_4^+	5.97	$H_2PO_4^-$	-6.16	$NiSO4$	2.18
Mg^{2+}	8.72	BrO_3^-	-4.89	$KFe(CN)6^{2-}$	-2.53
Ca^{2+}	8.88	NO_2^-	-3.85	$KFe(CN)6^{3-}$	-17.18
Sr^{2+}	8.76	NO_3^-	-3.66		
Ba^{2+}	8.50	ClO_3^-	-4.10		
Mn^{2+}	8.58	CKO_4^-	-3.60		
Co^{2+}	8.76	HCO_3^-	-5.32		
Ni^{2+}	8.47	HSO_4^-	-6.21		
Cu^{2+}	8.41	SO_4^{2-}	-13.20		
Zn^{2+}	8.76	$S_2O_3^{2-}$	-14.03		
Cd^{2+}	8.71	SO_3^{2-}	-13.12		
Pb^{2+}	8.40	CrO_4^{2-}	-13.69		
Fe^{2+}	9.33	$Cr_2O_7^{2-}$	-11.16		
Fe^{3+}	9.82	CO_3^{2-}	-13.22		
Al^{3+}	10.41	$Fe(CN)_6^{3-}$	-20.87		
Ce^{3+}	10.62	$Fe(CN)_6^{4-}$	-26.83		
Cr^{3+}	11.28				
La^{3+}	12.89				
Th^{4+}	12.42				

* from reference [4].

Table 2. Free Energy Parameter $(-\Delta\Delta.G/RT)i$ *Data for Some Inorganic Ions for Aqueous Solutions and Different Membrane Materials.* *

Ion	$(-\Delta\Delta G/RT)i$		
	Aromatic Polyamide	Aromatic Polyamide-Hydrazide	Cellulose Acetate-Propionate
Li^+	-1.77	-1.20	-1.25
Na^+	-2.08	-1.35	-1.30
K^+	-2.11	-1.28	-1.27
Rb^+	-2.08	-1.27	-1.23
Cs^+	-2.04	-1.23	-1.18
F^-	1.03	1.03	0.42
Cl^-	1.35	1.35	1.10
Br^-	1.35	1.35	1.15
I^-	1.33	1.33	1.20

* from reference [4]. Consult the original reference for the exact structure of the polymers used.

$$\ln (D_{AM}K/\tau)_{Org} = \ln C^*_{Org} + \rho^* \Sigma \sigma^*$$
$$+ \delta^* \Sigma E_s + \omega^* \Sigma s^* \qquad (5)$$

where $\Sigma \sigma^*$ is the Taft number [18] which represents the polar contribution, ΣE_s is the Taft steric number which represents the steric contribution, and Σs^* is the modified Small's number which repersents the nonpolar contribution. These three numbers are related to the physicochemical nature of the solute and as such they can be looked up in tables or estimated for most organic molecules [4,17]. The parameters ln C^*_{Org}, ρ^*, δ^*, and ω^* are parameters which are fit to the experimental data for any given membrane. Again ln C^*_{Org} is considered to represent the effect of the membrane pore size on the transport parameter.

To illustrate the use of this equation, consider the case of simple alcohol solutes in water with cellulose acetate membranes. For this case the polar nature of the solute is the dominating

factor and Equation (5) simplifies to:

$$\ln (D_{AM}K/\tau)_{Org} = \ln C^*_{Org} + \rho^* \Sigma \sigma^* \qquad (6)$$

This relationship is illustrated in Figure 11 for three different cellulose acetate membranes and 7 different alcohol solutes.

Using the concept of the free energy parameter it is possible to further modify Equation (5) as follows:

$$\ln (D_{AM}K/\tau)_{Org} = \ln C^*_{Org} + (-\Delta \Delta G/RT)$$
$$+ \delta^* \Sigma E_s + \omega^* \Sigma s^* \qquad (7)$$

where the free energy parameter for the solute can be calculated as a function of the organic molecule by a group contribution method [19]. Using a group contribution method facilitates the prediction of $D_{AM}K/\tau$ for a wide variety of different organic solutes from a knowledge of the solute chemical structure only.

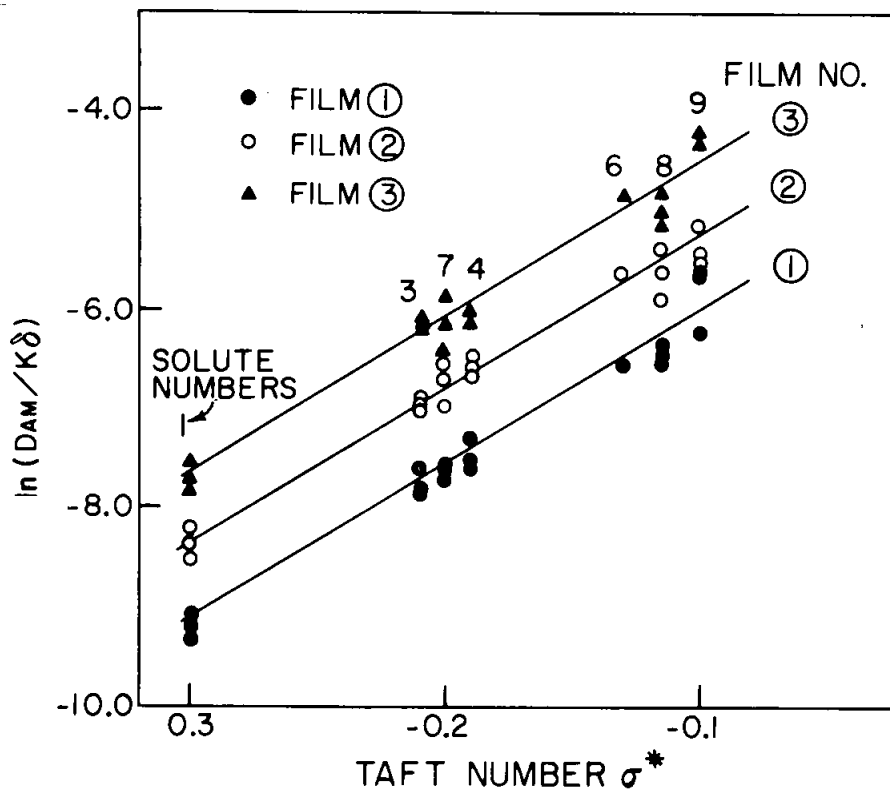In some cases, the solute transport

Figure 11. The relationship between the Taft number and the solute transport parameter for three different cellulose acetate membranes and 7 different alcohol solutes (with permission from reference [17]).
Solutes: 1=t-butanol;3=s-butanol; 4=i-propanol; 6=n-butanol; 7=i-butanol; 8=n-propanol; 9=ethanol.

parameter, $D_{AM}K/\tau$, is not constant [4,20] but varies with concentration and/ or pressure. One approach is to describe this dependence by some empirical correlation between $D_{AM}K/\tau$ and the operating conditions [20]. This method works, but the result is that several additional adjustable parameters must be introduced into the model. A better approach may be to try a different transport model. In reference 9 these two approaches are compared for some thin-film composite aromatic polyamide membranes.

Note that in the original papers by Sourirajan and coworkers, the values for $D_{AM}K/\tau$ are expressed in cm/s. To use the correlation is SI units (m/s), the various parameters and coefficients, such as

$$I_{M^{+}}, \ (-\Delta\Delta G/RT) \ \text{or} \ \delta^{*}$$

can be used directly. The only change requied is that $D_{AM}K/\tau$ and C^{*} should both be in m/s.

In summary the above analysis provides a useful way of correlating data for a wide variety of inorganic and organic solutes which then allows prediction of performance for almost any solute with that same membrane. The weaknesses in this analysis are as follows. The equations correlate a grouped parameter, $D_{AM}K/\tau$, which may or may not be constant for a given system and which may not behave as a single quantity. Furter, the parameters in the model are only known for a few types of membranes and therefore need to be determined experimentally for different membrane materials. Notwithstanding these problems, this analysis can be very useful once the initial work is invested in collecting enough data to determine the unknowns in the model.

An Algorithm for Solving the Transport Equations

Once the transport parameters, A, $D_{AM}K/\tau$, and k are determined (as shown above) then it is necessary to convert this information into flux and separation data for the desired operating conditions. This calculation is done by solving the transport Equations (6), (8), (12), and (34) of reference 1 simultaneously with knowledge of

the solution properties, density, viscosity, diffusivity and osmotic pressure. The degree of difficulty of this calculation depends on whether the feed solution can be considered dilute.

For dilute solutions the prediction is quite simple. First the definition of dilute solution is that the operating pressure is large compared to the osmotic pressure $(\Delta P \gg \Delta\pi)$ and the solvent flux is large compared to the solute flux $(N_B \gg N_A)$. The necessary equations can be simplified to:

$$f=\{1+\frac{D_{AM}K/\tau}{N_T}exp\left(\frac{N_t}{Ck}\right)\}^{-1} \qquad (8)$$

The total molar flux, N_T, can be approximated by the pure water molar flux, N_B, which is calculated from Equation (6) of reference 1 with $\Delta\pi=0$. The molar density, C, can be approximated by the molar density of pure water, 55.35 kmol/m^3 at 25°C.

For concentrated solutions the appropriate equations need to be solved simultaneously. A useful algorithm for this solution, provided that the molar density is approximately constant $(C=C_1=C_2=C_3)$, is presented here [21]. If the molar density is not constant then the governing equations can be rearranged to two equations in two unknowns, C_{A2} and C_{A3}, which can be solved by a Newton-Raphson technique.

In general the transport parameters, A, $D_{AM}K/\tau$, and k, the operating conditions, ΔP, and C_{A1}, the molar density, C, and the osmotic pressure versus concentration relationship, $\pi_i = \pi_i$ (C_{Ai}), are all known. Then Equations (6), (8), (12), and (27) of reference 1 can be rearranged as:

$$\frac{C_{A3}}{C_{A2}}=\frac{CD_{AM}K/\tau}{N_T+C(D_{AM}K/\tau)} \qquad (9)$$

$$\frac{C_{A1}}{C_{A2}}=\frac{C_{A3}}{C_{A2}}+\left(1-\frac{C_{A3}}{C_{A2}}\right)exp\left(-\frac{N_T}{Ck}\right) \qquad (10)$$

$$N_T=A(P-(\pi_2-\pi_3))+ $$
$$(D_{AM}K/\tau)(C_{A2}-C_{A3}) \qquad (11)$$

The trial and error method proceeds as follows:

1. Guess a reasonable value for N_T; $(N_T \cong A(\Delta P$

$-\pi_I$) is a good first guess).

2. Calculate C_{A3}/C_{A2} form Equation (9).
3. Calculate C_{A1}/C_{A2} form equation (10).
4. Calculate C_{A2} and C_{A3} from known ratios in steps 2 and 3 and the feed concentration C_{A1}.
5. Calculate the total flux N_T from Equation (11).
6. Compare calculated and guessed values of N_T and repeat steps 1 to 6 until the algorithm converges. Note that the calculated N_T (in step 6) is a good next guess.

The above algorithm converges very quickly—in 3 or 4 iterations—and is a considerable improvement over techniques suggested previously [2,4].

Solving the Transport Equations for the MD-SF-PF Model

The modified surface force-pore flow (MD-SF-PF) [6,7] is mathematically more complex than the KSA model and therefore requires the use of advanced numerical routines. For example, in Figure 2, the unknown parameters in the model are determined from data at 2000 ppm and these parameters are used to predict the effect of concentration on separation and flux. As shown in Figure 2, the agreement between data and model is excellent.

PREDICTION FOR MIXED SOLUTES

The prediction of preformance for mixed solute systems can be considerably more complex than the prediction for single solute systems. In general, there may be strong interactions between the various solutes and this leads to a complex relationship between operating conditions and performance.

Howere, for many mixed solute systems it is reasonable to assume that the solutes act independently of each other. In this case the transport equations are straight forward. Using, for example, the KSA model, the solute transport equation and the mass transfer equation for mixing on the high pressure side of the membrane can each be written for each of

solute species i (or each salt or individual ion i) in a complex mixture as:

$$N_T = C k_i ln\left(\frac{C_{i2}-C_{i3}}{C_{i1}-C_{i3}}\right) \qquad (12)$$

and

$$N_i = (D_{iM}K/\tau)(C_{i2} - C_{i3}) \qquad (13)$$

The solvent water flux, N_B, is similar to before except that the sum of the osmotic pressures of all the solutes must be considered:

$$N_B = A(\Delta P - \Sigma\Delta\pi_i) \qquad (14)$$

This equation predicts that the effective operating pressure is reduced due to the osmotic pressure of all the solutes. Consider the case of a two solute system, 0.01 % ethanol and 10 % sucrose, in water. The sucrose has a high osmotic pressure and therefore the effective pressure driving force is lower for both of the solutes. As a result the presence of the sucrose causes the ethanol separation to decrease even though concentration of the ethanol is small. The work of sourirajan and coworkers on this approach has been summarized in reference 22.

Very little has been published on mixed solute systems and even less has been published on systems where there is an interaction between the solute components such that they do not behave independently. Jonsson [23] examined multicomponent interactions using a model based on irreversible thermodynamics. More recently Thiel and Lloyd [24,25] have used the Stefan-Maxwell equations to describe the transport of multicomponent systems with possible interaction between the solutes.

OTHER COMPLICATIONS TO THE PREDICTION PROCESS

It is important to remember that the reviewed transport models [1] are restricted by the assumption and simplification used in their development. As a result it is not surprising that in some cases the models may not describe or predict experimental data very well. As a result it is sometimes necessary to modify the models. In this section three cases which can occur are briefly discussed.

Partially Dissociated solute Systems

The first case occurs when the solute present tends to partially dissociate so that ionized and nonionezed species are present in solution at the same time. This case can be treated as a mixed solute system where the ionized species are treated the same way as for inorganic solutes (see previous Section) and the nonionized (or ion—pair) species are treated as separate components. Therefore, there is a transport parameter for each of the different species present. As well, for species that are in equilibrium with each other the appropriate dissociation relationship can be written for the feed and permeate solutions. An example for partially dissociated organic acids is presented in reference 26. A similar analysis for inorganic solutes that form ion—pairs in solution is given in reference 4. Some free energy parameter data for inorganic ion—pairs and cellulose acetate membranes are presented in Table 1.

Strong Solute-Membrane Attraction

It has been shown that for many systems the solute may be strongly attracted to the membrane material. This attraction can cause anomalous reverse osmosis performance. For instance it is possible to observe negative separation, indicating that the solute is enriched in the permeate stream; in many cases the separation tends to decrease (instead of increase) with increasing operating pressure; and often the permeate flux is significantly reduced from the pure water flux even if the solution is dilute so that osmotic pressure effects are negligible. A common example, that exhibits the above behavior is for phenol, phenol derivative, and hydrocarbon solutes with cellulose acetate membranes [13, 27, 28]. A review of this type of behavior and some attempts at modeling the experimental data are presented elsewhere [28].

Charged Membranes

The models discussed in the previous paper [1] are applicable for a wide variety of solutes in membranes that are essentially neutral in character. However, unusual behavior can be observed with charged solutes in membranes containing fixed charged groups [29,30]. For instance, the membrane can exchange ions between the feed solution and the ion exchange groups on the membrane. This can lead to swelling (or shrinking) of the membrane structure which in turn effects the transport properties of the membrane. As a first approximation the methods in this chapter can be used, but the transport parameters may be a strong function of the operating conditions.

CONCLUSION

The main conclusions of this paper are as follows. The effects of operating conditions on reverse osmosis membrane preformance has been reviewed, and it has been shown how to use a transport model to predict these effects. Based on semiempirical relationships it is possible to predict the performance for new solutes that have not been previously tested from knowledge of the structure of the solute only. The transport models can be extended to mixed solute systems but little work has been done in this area. Finally, these models, with the exception of the MD-SF-PF model, may fail in their ability to describe performance for certain systems such as those where there is strong attraction between the solute and the membrane material.

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NOMENCLATURE

A	Pure water permeability coefficiecnt ,kmol/m² s kPa.
A_o	Constant defined in Equation (1), kmol/m²s kPa.
A_o	Pure water permeability coefficient extrapolated to zero operating pressure,kmol/m² s kPa.
C	Molar density, kmol/m³.
C_{ij}	Molar concentration of component i

at location j, kmol/m^3.

C^*_i Membrane pore size parameter with reference to the solute i as defined by Equation (2) or (5), m/s.

D_{ij} Diffusivity of component i in component j, m^2/s.

$(D_{iM}K/t)_i$ Solute transport parameter for solute i, m/s.

E_o Apparent activation energy for solvent transport, kJ/kmol.

$\sum E_s$ Taft steric number.

f Separation.

$(-\Delta\Delta G/RT)_i$ Free energy parameter for solute i.

I_i Free energy parameter component i.

K Solute partition coefficient.

k Mass transfer coefficient, m/s.

k_i Mass transfer coefficient for component i, m/s.

n_a Number of anions in the salt formula.

n_c Number of cations in the salt formula.

N_i Molar flux of component i, kmol/m^{2}s.

ΔP Pressure difference across the membrane, kPa.

R Gas constant, KJ/kmol K.

$\sum s^*$ Modified Small's number.

T Temperature, K.

Greek Symbols

δ^* Steric parameter in Equation (5).

π_i Osmotic pressure of solution i, kPa.

$\Delta\pi$ Osmotic pressure difference across the membrane, kPa.

ρ^* polar parameter defined by Equation (5).

$\sum\sigma^*$ Taft number.

ω^* Nonpolar parameter defined by Equation (5).

ι Effective pore length, m.

Subscripts

A   solute
B   solvent
M   membrane
M^+ cation in MX
MX   salt MX

NaCl   sodium chloride
Org   organic
T   total solution
X$^-$ anion in MX
1   feed solution
2   boundary layer solution
3   permeate solution

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