Fundamentals of RO Membrane Separation Process: Problems and Solutions

Ahmad Fauzi Ismail[a] & Takeshi Matsuura[b*]

[a]Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Department of Chemical and Biological Engineering, University of Ottawa, 161 Louis Pasteur St, Ottawa, ON K1N 6N5, Canada

ABSTRACT

It is the intention of the authors to let the students understand the underlying principles of membrane separation processes by solving the problems numerically, in general. In particular, in this article problems and answers are presented for reverse osmosis (RO), one of the membrane separation processes driven by the transmembrane hydraulic pressure difference. The transport theories for RO were developed in early nineteen sixties, when the industrial membrane separation processes emerged. These problems are solved step by step using a simple calculator or Excel in computer.

Keywords: Reverse osmosis, theory, separation, hydraulic pressure

1.0 INTRODUCTION

While the authors were teaching the membrane courses at Universiti Teknologi Malaysia and University of Ottawa, they realized the need for a text book, by which the students can learn the fundamental theories by solving the problems without having complicated software. Although a number of books have been published so far on the membranes and membrane separation processes, the authors have not found any books in which membrane related problems and solutions are assembled. This article is written, therefore, to address such a need.

All the problems given in this paper are so designed that they can be solved by using a simple calculator or Excel in the computer, as the authors believe that the students can better understand the fundamentals by solving simple questions.

At the end of the last millennium, membrane separation processes were rather limited to the pressure driven processes such as reverse osmosis (RO), ultrafiltration (UF), microfiltration (MF), membrane gas separation and pervaporation, as well as electrodialysis. During the last two decades, the scope of the R&D of membrane separation processes has been significantly broadened. In addition to the above-mentioned separation processes, possibilities of applying forward osmosis (FO), pressure retarded osmosis (PRO), membrane distillation (MD), membrane contactor, membrane adsorption etc. for energy and cost reduction have been examined. Most importantly, the hybrid systems in which two or more membrane systems are combined are now being investigated for large scale applications.

In this article, problems-solutions are assembled only for RO. It is the authors' intention to add the other membrane separation processes in the future articles in Journal of Applied Membrane Science and Technology (AMST). Therefore, even though this article includes only one chapter, which is RO, the chapter is called Chapter 1. The other chapters will appear in AMST in the future.

2.0 REVERSE OSMOSIS

2.1 Reverse Osmosis Performance

When the aqueous solutions of two different salt concentrations are separated by a semipermeable membrane, which allows the transport of solvent but does not allow the transport of salt, there is a natural tendency for water flow from the solution of the lower concentration to the solution of the higher concentration. The driving force for the solvent flow is the difference in osmotic pressure. This phenomenon is called osmosis (Figure 1a).

However, when a hydraulic pressure that is higher than the osmotic pressure is applied on the solution of the higher salt concentration, the direction of the flow is reversed. This phenomenon is called reverse osmosis (Figure 1c).

The semipermeable membrane is often not perfect and a small amount of salt diffuses from the higher salt concentration to the lower salt concentration.

According to the solution diffusion model, the RO transport is given as:

$$J_A = A(\Delta p - \Delta \pi)$$
(1)

where J_A is solvent (mostly water) flux, Δp and $\Delta \pi$ are the difference in

hydraulic and osmotic pressure, respectively, between both sides of the semipermeable membrane, and the difference, Δ, is defined as (right side – left side in Figure 1). In Equation (1) $\Delta p - \Delta \pi$ is, therefore, considered as the driving force for the water flow from the right to left side. A is a proportionality constant called water permeation coefficient. As for solute,

$$J_B = B \Delta c$$
(2)

where J_B is the solute flux and Δc is the difference in concentration between both sides of the membrane. Again, the difference Δ is defined as (right side - left side). Therefore, Δc is always positive and the solute flux is also from right to left. B is a constant called solute permeation constant.

Furthermore, Lonsdale *et al*. has shown that,

$$J_A = \frac{c_{Am} D_{Am} v_A}{RT d}(\Delta p - \Delta \pi)$$
(3)

where c_{Am} is the concentration of water in the membrane, D_{Am} is the diffusion coefficient of water in the membrane, v_A is the molar volume of water and δ is the membrane thickness [1]. And,

$$B = \frac{D_{Bm} K_B}{d}$$
(4)

where, D_{Bm} is the diffusion coefficient of solute in the membrane, K_B is the distribution constant of solute between water and membrane.

In reverse osmosis, the important performance parameters are the solvent flux, which is given by Equation (3) and the solute separation, f', defined as;

$$f' = 1 - \frac{c_{B3}}{c_{B2}}$$
(5)

c_{B2} and c_{B3} are the solute concentration at the high-pressure side (i.e. the right side in Figure 1b) and the low-pressure side (i.e. the left side in Figure 1b).
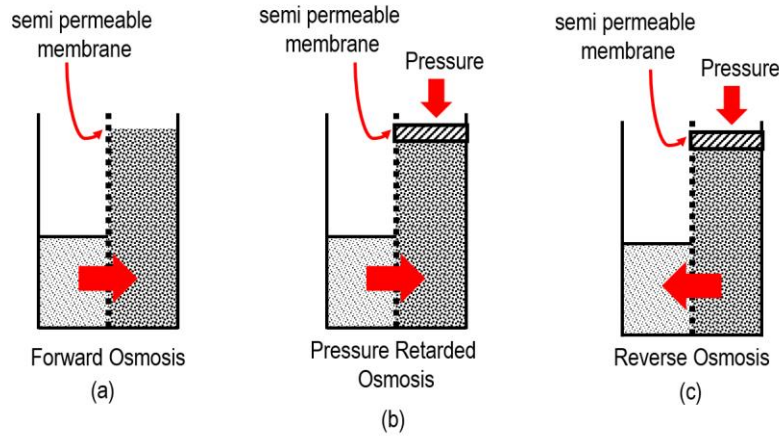
Figure 1 Forward osmosis, pressure retarded osmosis and reverse osmosis

The solute separation can be further given by:

$$f' = \frac{1}{1 + \dfrac{D_{Bm}K_B RT c_{A3}}{D_{Am}c_{Am}v_A(p_2 - p_3 - p_2 + p_3)}} \quad (6)$$

Problem:
The following data were given by Lonsdale [1].

$D_{Am}c_{Am} = 2.7 \times 10^{-8}$ kg/m s, and;

$D_{Bm}K_B = 4.2 \times 10^{-14}$ m^2/s.

Calculate the solute separation of sodium chloride based on molality and the water flux, when the feed sodium chloride molality is 0.1 and the operating pressure, $\Delta p = p_2 - p_3$, is 4.134×10^6 Pa. The thickness of the membrane is 10^{-7} m. Use the following numerical values:

$RT = 2.479 \times 10^3$ J/mol at 25°C;

$c_{A3} = 10^3$ kg/m^3, and;

$v_A = 18.02 \times 10^{-6}$ m^3/mol.

Answer:
The coefficient for the osmotic pressure = 2.5645×10^8 Pa per mole fraction.

The molality of sodium chloride is 0.1, which means that 0.1 mole of NaCl is dissolved in 1 kg of water. Hence, the mole fraction of NaCl is;

$$\frac{0.1}{0.1 + \left(\dfrac{1000}{18.02}\right)} = 1.799 \times 10^{-3}$$

The osmotic pressure (Pa) is;

$$(2.5645 \times 10^8) \times (1.799 \times 10^{-3}) = 0.461 \times 10^6$$

Iteration is necessary to calculate the solute separation and flux.

First, solute concentration in the permeate is assumed to be zero.

Therefore, $\pi_2 - \pi_3 = 0.461 \times 10^6$ Pa

From Equation (6);

$$f' = \left[1 + \frac{(4.2 \times 10^{-14})(2.479 \times 10^3)(10^3)}{(2.7 \times 10^{-8})(18.02 \times 10^{-6} - 0.461 \times 10^6)}\right]^{-1} = 0.954$$

Then the solute molality in the permeate becomes;

$0.1 \times (1-0.945) = 0.0055$

The mole fraction of the permeate is;

$$\frac{0.0055}{0.0055 + \dfrac{1000}{18.02}} = 9.910 \times 10^{-5}$$

The osmotic pressure (Pa) of the permeate is;

$(2.5645 \times 10^8) \times (9.910 \times 10^{-5}) = 0.0254 \times 10^6$

$\pi_2 - \pi_3 \ (0.461 - 0.0254) \times 10^6 = 0.4356 \times 10^6$

Using the osmotic pressure newly obtained;

$$f' = \left[1 + \frac{(4.2 \times 10^{-14})(2.479 \times 10^3)(10^3)}{(2.7 \times 10^{-8})(18.02 \times 10^{-6})(4.134 \times 10^6 - 0.4356 \times 10^6)} \right]^{-1} = 0.945$$

$f' = 0.945$ is therefore accurate enough. The water flux (kg/m^2 s) is from Equation (3):

$$J_A = \frac{(2.7 \times 10^{-8})(18.02 \times 10^{-6})(4.134 \times 10^6 - 0.4356 \times 10^6)}{(2.479 \times 10^3)(10^7)} = 72.56 \times 10^{-4}$$

When there is no solute in the feed, there is no osmotic pressure effect. Therefore,

$$J_A = \frac{(2.7 \times 10^{-8})(18.02 \times 10^{-6})(4.134 \times 10^6)}{(2.479 \times 10^3)(10^7)} = 81.14 \times 10^{-4}$$

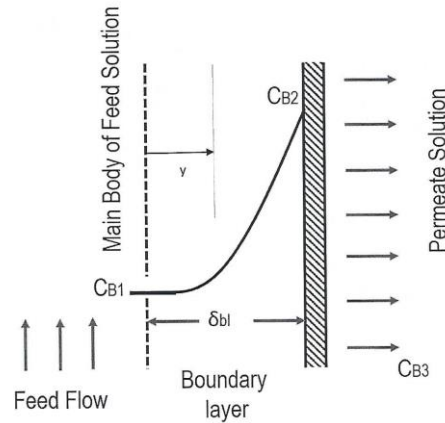## 2.2 Concentration Polarization

When water permeates through the membrane preferentially from the feed to the permeate, the salt is left behind near the membrane on the feed side unless salt diffuses back to the main body of the feed solution. This phenomenon is called concentration polarization that causes negative effects on membrane performance such as flux and selectivity reduction. According to the boundary layer theory, concentration polarization is described as follows.

First, the presence of the boundary layer of thickness, δ_{bl} is assumed so that the salt diffusion from the membrane to the main body of the feed stream occurs in the boundary layer (see Figure 2; Note water flow is reversed in Figure 2, i.e. water flows from left to right). When the mass balance between the plane at a distance y and the membrane wall at a distance δ_b is considered,

$$-D_{BA} \frac{dc_B}{dy} + vc_B = vc_{B3} \tag{7}$$

where D_{BA} is the diffusion coefficient (m^2/s) of solute B in solvent A in the boundary layer, c_B is the solute concentration and v is the solution velocity.

The first and second terms of the left-hand side of the equation is the diffusive and convective flow of the solute into a plane at the distance y and the right-hand side is the solute flow from the permeate side of the membrane. They should be equal at the steady state.

Figure 2 Concentration polarization

Rearranging Equation (7)

$$\frac{dc_B}{dy} = \frac{v}{D_{BA}}(c_B - c_{B3}) \tag{8}$$

Then,

$$\frac{dc_B}{c_B - c_{B3}} = \frac{v}{D_{BA}} dy \tag{9}$$

Integrating

$$\ln(c_B - c_{B3}) = \frac{v}{D_{BA}} y + C \tag{10}$$

where C is the integral constant.

Since $c_B = c_{B1}$, at y = 0 (see Figure 2)

$$\ln(c_{B1} - c_{B3}) = C \tag{11}$$

Substituting in Equation (11) for Equation (10);

$$\ln\frac{c_B - c_{B3}}{c_{B1} - c_{B3}} = \frac{v}{D_{BA}} y \tag{12}$$

Since $c_B = c_{B2}$, at y = δ_{bl} (see Figure 2)

$$\ln\frac{c_{B2} - c_{B3}}{c_{B1} - c_{B3}} = \frac{v}{D_{BA}} d_{bl} \tag{13}$$

Defining the mass transfer coefficient as

$$k = \frac{D_{BA}}{d_{bl}} \tag{14}$$

Equation (13) becomes

$$\ln\frac{c_{B2} - c_{B3}}{c_{B1} - c_{B3}} = \frac{v}{k} \tag{15}$$

The boundary concentration, c_{B2}, cannot be obtained experimentally but can be calculated using Equation (15) by knowing c_{B1}, c_{B3}, v and k. c_{B1}, c_{B3}, v is known experimentally and k is often evaluated by dimension analysis.

It should be reminded that the solute separation, f', was defined as

$$f' = 1 - \frac{c_{B3}}{c_{B2}} \tag{5}$$

It is impossible to obtain f' experimentally, since c_{B2} cannot be known by experiment. f' can be known only by using Equation (15) by which c_{B2} can be calculated. Another solute separation:

$$f' = 1 - \frac{c_{B3}}{c_{B1}} \tag{16}$$

is used more often. In Equation (16) c_{B1} is known experimentally when the feed solution is prepared. It should be noted however f is not, but f' is the intrinsic property of the membrane.

2.3 Prediction of RO Performance Considering Concentration Polarization

Prediction of RO performance considering the concentration polarization was attempted by Kimura and Sourirajan [2]. Unlike Lonsdale's derivation that is based on weight-based concentration (kg/m^3) and flux (kg/m^2 s), Kimura-Sourirajna's equations are based on molar concentration (mol/m^3) and molar flux (mol/m^2 s). But other than that, the equations similar to Equations (1) and (2) are used.

From section 1.2. it is now clear that the solute concentration at the feed solution/membrane interface, called boundary concentration (c_{B2}) is different from that of the main body of the feed, called bulk feed concentration, c_{B1}. Hence, from now on, the subscripts 1, 2 and 3 are used for the bulk feed, the boundary and the permeate. Since in Equation (1) Δ

means the difference between feed solution/membrane interface, 2, and permeate solution/membrane interface, 3, the equation can be rewritten as:

$$J_A = A(p_2 - p_3 - \rho_2 + \rho_3) \qquad (17)$$

(Note that pressure does not change from the bulk feed to the feed solution/membrane interface, hence $p_1 = p_2$. As well, pressure and concentration do not change from the permeate solution/membrane interface to the bulk permeate.)

Similarly, the solute flux is:

$$J_A = B(c_{B2} - c_{B3}) \qquad (18)$$

Furthermore,

$$c_{B1} = c_1 X_{B1} \qquad (19)$$
$$c_{B2} = c_2 X_{B2} \qquad (20)$$
$$c_{B3} = c_3 X_{B3} \qquad (21)$$

where c is the total molar concentration including solvent and

solute and X_B is the mole fraction of the solute.

Substituting Equations (20) and (21) for c_{B2} and c_{B3} in Equation (18),

$$J_B = B(c_2 X_{B2} - c_3 X_{B3}) \qquad (22)$$

Also using the relation:

$$\frac{J_B}{J_A + J_B} = X_{B3} \qquad (23)$$

$$J_A = B\left(\frac{1 - X_{B3}}{X_{B3}}\right)(c_2 X_{B2} - c_3 X_{B3}) \qquad (24)$$

Using Equation (15) for concentration polarization, and assuming

$$c_1 = c_2 = c_2 = c \qquad (25)$$

since the molar concentration of water is much greater than the salt concentration in the aqueous solution, and also with the relation:

$$v = \frac{J_A + J_B}{c} \qquad (26)$$

Table 1 Osmotic pressure data pertinent to different electrolyte solutions (at 25°C, kPa)

Molality	NaCl	LiCl	KNO$_3$	MgCl$_2$	CuSO$_4$
0	0	0	0	0	0
0.1	462	462	448	641	276
0.2	917	931	862	1303	510
0.3	1372	1407	1262	1999	731
0.4	1820	1889	1648	2737	945
0.5	2282	2386	2020	3523	1165
0.6	2744	2889	2379	4357	1379
0.7	3213	3413	2737	5233	1593
0.8	3682	3944	3082	6178	1813
0.9	4158	4482	3427	7191	2055
1.0	4640	5040	3750	8266	2302
1.2	5612	6191	4385	10611	2834
1.4	6612	7398	4992	13231	3434
1.6	7646	8646	5557	16127	-

Equation (15) is rearranged to

$$J_A = ck(1 - X_{B3})\ln\frac{X_{B2} - X_{B3}}{X_{B1} - X_{B3}} \qquad (27)$$

Problem:
Under the following RO experimental conditions;

Feed: Aqueous NaCl solution
Feed molality: 0.6
Operating pressure: 10,335 kPa gauge
Effective membrane area: 13.2×10^{-4} m^2
The following data were obtained.
Pure water permeation rate: 159.8×10^{-3} kg/h
Permeation rate for the feed NaCl solution: 122.9×10^{-3} kg/h
Solute separation based on molality, 81.2 %.

Calculate parameters A, B and k, using the following numerical values,

$$c_1 = c_2 = c_3 = c = 55.3 \text{ kmol/m}^3 \quad (28)$$

Molecular weight of NaCl = 58.45 kg/kmol

Answer:
The flux of pure water is;

$$J_{A=}\frac{(159\times10^{-3})}{(18.02)\times(13.2\times10^{-4})(3600)}$$

$= 1.867 \times 10^{-3}$ kmol/m^2 s

In Equation (17), π_2 and π_3 are equal to zero, therefore,

$$A=\frac{1.867\times10^{-3}}{10,355}$$

$= 1.806 \times 10^{-7}$ kmol/m^2 s kPa

As for the flux for the NaCl feed solution,

The permeate molality is

$(0.6)(1 - 0.812) = 0.1128$ molal

0.1128 mol of NaCl (0.1128×10^{-3}) $(58.45) = 6.593 \times 10^{-3}$ kg) is in 1 kg of water, then in 122.9×10^{-3} kg of the permeate, the amount of water is

$$122.9\times\frac{1}{1+(6.593\times10^{-3})}$$

$= 122.1 \times 10^{-3}$ kg

Therefore, water flux is:

$$JA=\frac{(122.1\times10^{-3})}{(18.02)(13.2\times10^{-4)}(3600)}$$

$= 1.426 \times 10^{-3}$ kmol/m^2 s

From Table 1 the osmotic pressure corresponding to the permeate molality of 0.1128 molal is 520 kPa.

From Equation (17),

$$P_2 = p_2 - p_3 + P_3 - \frac{J_A}{A} \qquad (29)$$

Inserting numerical values,

$$\pi_{2=}10,355+520 - \frac{1.426\times10^{-3}}{1.806\times10^{-7}}$$

$= 2957$ kPa

From Table 1 the molality of at the feed solution/membrane interface is 0.6459.

Therefore, the mole fractions are,

$$XB_1 = \frac{0.6}{0.6 + \dfrac{1,000}{18.02}} = 0.01070$$

,

$$XB_2 = \frac{0.6459}{0.6457 + \dfrac{1,000}{18.02}} = 0.01150$$

,

$$XB_3 = \frac{0.1128}{0.1128 + \dfrac{1,000}{18.02}} = 0.002029$$

Rearranging with Equation (24) with the approximation, Equation (28),

$$B = \frac{J_A}{c\left[\dfrac{(1 - X_{B3})}{X_{B3}}\right](X_{B2} - X_{B3})} \tag{30}$$

Inserting numerical values,

$$B = \frac{(1.426 \times 10^{-3})}{(55.3)\left[\dfrac{(1 - 0.002029)}{0.002029}\right](0.01150 - 0.002029)}$$

$$= 5.536 \times 10^{-6} \text{ m/s}$$

Rearranging Equation (27)

$$k = \frac{J_A}{c(1 - X_{B3})\ln\dfrac{X_{B2} - X_{B3}}{X_{B1} - X_{B3}}} \tag{31}$$

Inserting numerical values,

$$k = \frac{(1.426 \times 10^{-3})}{(55.3)(1 - 0.002029)\ln\dfrac{(0.01150 - 0.002029)}{(0.01070 - 0.002029)}}$$

$$= 292.8 \times 10^{-6} \text{ m/s}$$

Problem:
For a given set of parameters,

$A = 3.04 \times 10^{-7}$ kmol/m^2 s kPa
$B = 8.03 \times 10^{-7}$ m/s
$k = 22 \times 10^{-6}$ m/s

calculate the solute separation, f, pure water flux, permeate flux when the feed is 0.6 molal NaCl solution and the operating pressure is 6895 kPa (gauge). Assume that Equation (25) is valid and the osmotic pressure is proportional to NaCl mole fraction.

Answer:
Equations (17) and (24) under the assumption (Equation (25))

$$A(p_2 - p_3) - A\rho°(X_{B2} - X_{B3})$$
$$= Bc\left[\frac{(1 - X_{B3})}{X_{B3}}\right](X_{B2} - X_{B3}) \tag{32}$$

Where π^o is the proportional constant between π and X_B. Rearranging,

$$X_{B2} - X_{B3} = \frac{A(p_2 - p_3)}{A\rho° + Bc\left[\dfrac{(1 - X_{B3})}{X_{B3}}\right]} \tag{33}$$

From Equation (17) and (27)

$$A(p_2 - p_3) - A\rho°(X_{B2} - X_{B3})$$
$$= ck(1 - X_{B3})\ln\frac{X_{B2} - X_{B3}}{X_{B1} - X_{B3}} \tag{34}$$

Inserting the numerical values,

$$A(p_2 - p_3) = (3.04 \times 10^{-7})(6,895 - 0)$$

$$= 20,961 \times 10^{-7} \text{ kmol/m}^2 \text{ s}$$

Which is the pure water permeation flux. Since the osmotic pressure of 0.6 molal NaCl solution ($X_{B1} = 0.0107$) is 2744 kPa (see Table 1)

$$\rho° = \frac{2,744}{0.0107}$$

$$= 256,449 \text{ kPa}$$

Therefore,

$A\pi° = (3.04 \times 10^{-7})(256,449)$

$= 779,600 \times 10^{-7}$ kmol/m^2 s

Furthermore,

$Bc = (8.03 \times 10^{-7})(55.3)$

$= 444,06 \times 10^{-7}$ kmol/m^2 s

and,

$kc = (22 \times 10^{-6})(55.3)$

$= 12,166 \times 10^{-7}$ kmol/m^2 s

Inserting the above numerical values in Equation (33)

$$X_{B2} - X_{B3}$$

$$= \frac{(20,961 \times 10^{-7})}{(779,600 \times 10^{-7}) + (444.06 \times 10^{-7})\left[\frac{(1 - X_{B3})}{X_{B3}}\right]} \quad (35)$$

Also, inserting the above numerical values in Equation (34)

$(20,961 \times 10^{-7}) - (779,600 \times 10^{-7})(X_{B2} - X_{B3})$

$$= (12,166 \times 10^{-7})(1 - X_{B3})\ln\frac{X_{B2} - X_{B3}}{X_{B1} - X_{B3}} \quad (36)$$

Solving Equations (35) and (36) for 2 unknowns X_{B3} and $X_{B2} - X_{B3}$,
$X_{B3} = 0.00107$ and $X_{B2} - X_{B3} = 0.01755$

Then,

$$f = \frac{0.0107 - 0.00107}{0.0107} = 0.90$$

$J_A = A(p_2 - p_3) - A\pi°(X_{B2} - X_{B3})$

$= (20,961 \times 10^{-7}) - (779,600 \times 10^{-7})(0.01755)$

$= 7,280 \times 10^{-7}$ kmol/m^2 s

2.4 Pore Models

2.4.1 Preferential Sorption-capillary Flow Model

According to Sourirajan's book, the following fundamental equation called the Gibbs Adsorption Isotherm was the basis for the earliest development of reverse osmosis membrane at the University of California Los Angeles (UCLA) [3].
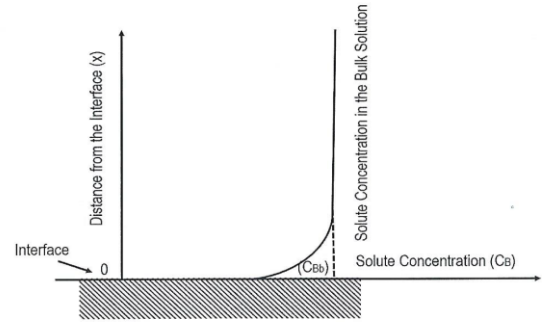
Figure 3 Solute concentration profile at the interface showing negative adsorption

In Figure 3, an interface is between two phases, one the shaded phase, representing air, and the other unshaded phase, representing NaCl solution. Upward far away from the interface the solution becomes the bulk solution whose concentration is c_{Bb}. But near the interface the concentration c_B is below c_{Bb}. Such an abrupt change of NaCl concentration at the interface is predicted by the Gibbs Adsorption Isotherm,

$$\Gamma = -\frac{1}{RT}\frac{\partial\sigma}{\partial\ln a} \quad (37)$$

where R is universal gas constant, T is absolute temperature, σ is surface tension and a is activity.

Γ is surface excess given by

$$\Gamma = \int_0^\infty (c_B - c_{Bb})dx \quad (38)$$

x is the distance from the interface.

**Table 2** Some physicochemical data pertinent to sodium chloride solution

Molality	Activity coefficient	Density $\times 10^{-3}$ (kg/m³)	Surface tension $\times 10^3$ (J/m²)
0.0000	-	-	72.80
0.2010	0.751	1.00675	73.17
0.5030	0.688	1.01876	73.71
1.0204	0.650	1.0385	74.515
2.0988	0.614	1.06984	76.27
3.1920	0.714	1,1152	78.08
4.3628	0.790	1.1507	80.02
4.9730	0.848	1.1679	81.09
5.5410	0.874	1.1947	82.17

Table 3 Physicochemical data of sodium chloride solution based on the data given in Table 2

αm (mol/kg)	$\gamma \times 10^3$ (J/m²)	$d\gamma/d(\alpha m) \times 10^3$	α	$\rho \times 10^{-3}$ (kg/m³)	m (mol/kg)	$t_i \times 10^{10}$ (m)
0	72.80	2.74[a]	1.0	1.0	0	5.62
0.5	74.16	2.70	0.669	1.024	0.747	3.78
1.0	75.50	2.52	0.624	1.056	1.603	3.35
1.5	76.68	2.15	0.616	1.081	2.435	2.87
2.0	77.65	1.82	0.640	1.103	3.125	2.57
2.5	78.50	1.67	0.685	1.122	3.650	2.54
3.0	79.32	1.62	0.745	1.139	4.027	2.68
3.5	80.12	1.58	0.795	1.152	4.403	2.82
4.0	80.90	1.49	0.833	1.164	4.802	2.79
4.5	81.61	1.35[b]	0.861	1.179	5.226	2.64

[a] = -3 x 72.80+4 x 74.16-75.50
[b] =80.12-4 x 80.9+3 x 81.61
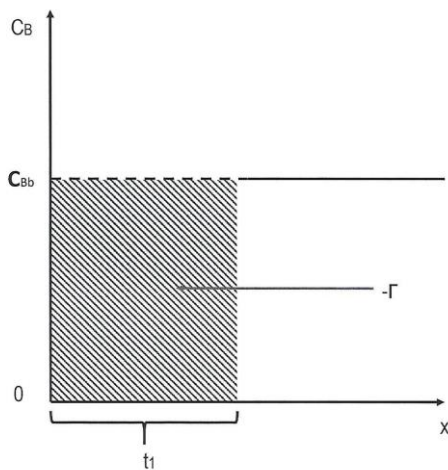
Figure 4 Assumption of a stepwise function for the solute concentration profile at the interface
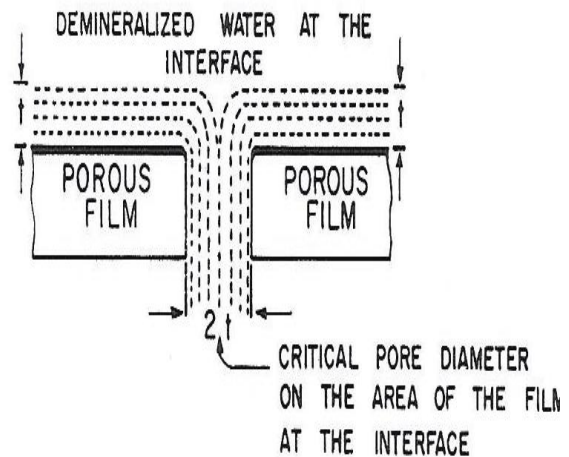
Figure 5 Preferential Sorption-Capillary Flow model

These equations predict the presence of a very thin pure water layer at the surface of NaCl.

Problem:

Activity coefficient, density, and interfacial tension of aqueous NaCl solutions at 20°C are given for different molalities in Table 2.

Calculate the interfacial pure water thickness using the data in Table 2.

Modification of Equation (37) is necessary.

For the solution of symmetric electrolytes,

$$a_{\pm} = a^{1/2} \tag{39}$$

Combining Equations (37) and (39)

$$
\begin{aligned}
G &= -\frac{1}{2RT}\left(\frac{\partial s}{\partial a_{\pm}}\right)_{T,A} \\
&= -\frac{1}{2RT}\left(\frac{\partial s}{\partial (\ln(am_{\pm}))}\right)_{T,A} \\
&= -\frac{am_{\pm}}{2RT}\left(\frac{\partial s}{\partial (am_{\pm})}\right)_{T,A} \\
&= -\frac{am}{2RT}\left(\frac{\partial s}{\partial (am)}\right)_{T,A}
\end{aligned}
\tag{40}
$$

Since

$$c_{Bb} = \frac{1,000m}{1,000 + 58.45m}\, r \tag{41}$$

where c_{Bb} is the bulk molar concentration of sodium chloride (mol/L).

Then,

$$
\begin{aligned}
&-\frac{G}{c_{Bb}} \\
&= -\frac{a(1,000 + 58.54m)}{2RT\, r \times 1,000}\left(\frac{\partial s}{\partial (am)}\right)_{T,A}
\end{aligned}
\tag{42}
$$

Assuming a stepwise concentration profile at the interface, as illustrated in Figure 4, and considering that $-\Gamma$ is equal to the shadowed area in the figure, $-\dfrac{\Gamma}{c_{Bb}}$ is the thickness of the layer where sodium chloride concentration is equal to zero.

Hence,

$$t_i = -\frac{G}{c_{Bb}} \tag{43}$$

The pure water thicknesses so calculated are given in Table 3. According to Sourirajan's Preferential Sorption-Capillary Flow model, the pure water formed at the salt water/membrane interface is driven by the pressure applied on the feed salty water through sub-nanometer sized pores. (Figure 5).

2.4.2 Glückauf Model

There are also a number of papers where the RO transport is discussed assuming the presence of pore. One of those is the Glückauf model [4].

Suppose water phase of dielectric constant D (dimensionless) and the polymer phase of dielectric constant D' are in contact with each other and there is a pore of radius r in the polymer phase. When an ion enters the pore, the potential of the ion steadily increases and it reaches a maximum value at the mean distance of the ionic cloud, $1/\kappa$, according to the Debye-Hückel model (Figure 6). When this distance is exceeded, an ion of the opposite charge will enter the pore, reducing the

potential of the first ion due to the ion-pair formation. The work required to bring the ionic particle to the distance of $1/\kappa$ from the pore entrance, $\Delta W''$, was approximated by the work required to bring the ion into the cavity of spherical shape shown in Figure 7 and it was given by

$$\mathrm{D}W'' = \frac{NZ^2 \in^2}{8\rho D(8.854 \times 10^{-12})} \frac{(1-a)Q}{r+abQ} \tag{44}$$

where Q is D/D', α is the fraction of solid angles over the whole sphere, as shown in Figure 7, which can be given by
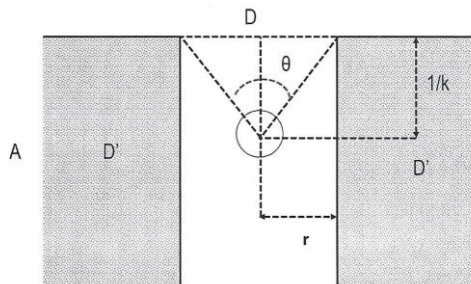
$$a = 1 - (1 + k^2 r^2)^{-1/2} \tag{45}$$

and b is the ionic radius.

The probability of finding the ion at this energy level is $exp(-\Delta W''/RT)$ Thus, the concentration in the pore is $c_{B2}exp(-\Delta W''/RT)$. ($c_{B2}$ is the salt concentration near the feed solution/membrane interface).

Assuming the concentration in the pore is equal to the permeate concentration, c_{B3},

$$c_{B3}$$
$$= c_{B2}\exp\left(\frac{NZ^2 \in^2}{8\rho D(8.854 \times 10^{-12})} \frac{(1-a)Q}{r+abQ}\right) \tag{46}$$

Figure 6 Ion is at the distance $1/\kappa$ from the pore entrance
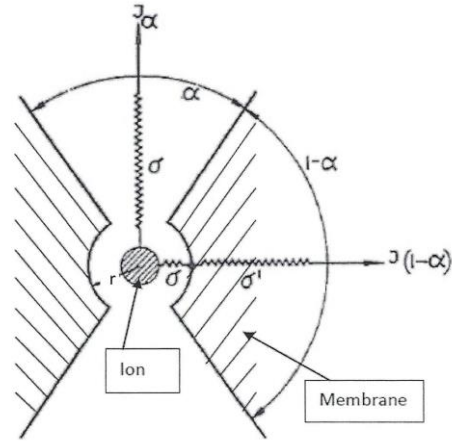
Figure 7 Glückauf model

Problem:
i) Given the following numerical values, calculate solute separation for pore sizes 0.3, 0.5, 0.7 and 1.0 nm using the Glückauf model for the feed NaCl solution of 1 mol/L.
ii) Calculate the solute separation of NaCl for the pore size of 0.5 nm when the feed NaCl concentration is 0.5 mol/L.
iii) Calculate the solute separation of MgSO$_4$ for the pore size of 0.5 nm when the MgSO$_4$ concentration is 1.0 mol/L.

Avogadro number
$N = 6.023 \times 10^{23}$ mol^{-1}
Valence for Na$^+$ and Cl$^-$ = 1, for Mg^{2+} and SO$_4{}^{2-}$ = 2
Electric charge $\varepsilon = 1.602 \times 10^{-19}$ C
Dielectric constant of water
$D = 78.54$ at 25 °C.
An average of dielectric constant of cellulose acetate $D' = 3.7$
Gas constant $R = 8.314$ JK^{-1}mol^{-1}
Absolute temperature T = 298.2 K
Average of ionic radii of Na$^+$ and Cl$^-$, $b = 0.142$ nm
Average of ionic radii of Mg^{++} and SO^{4-}
$b = 0.1525$ nm

Table 4 Solute separation calculated for different salts, salt concentrations and different pore sizes

Solute	Solute concentration (mol/L)	Pore radius $\times 10^{10}$ (m)	f'
NaCl	1	3	0.9902
NaCl	1	5	0.8684
NaCl	1	7	0.6994
NaCl	1	10	0.5058
NaCl	0.5	5	0.9593
MgSO$_4$	1	5	0.9391

$\frac{1}{k}$ is given as

$$\frac{1}{k} = \sqrt{\frac{D k_B T}{2 r_o N e^2}} I^{-1/2} \tag{47}$$

where k_B is the Boltzmann constant and ρ_0 is density of water. I is the ionic strength given as

$$I = \frac{1}{2} \sum_i c_i Z_i^2 \tag{48}$$

where c_i and Z_i are ionic concentration and ionic valence, respectively.

$$\frac{1}{k} = 3.05 \times 10^{-10} I^{1/2} \tag{49}$$

Can be used instead of Equation (47).

Answer:
For NaCl 1 mol/L solution

$$I = \frac{1}{2}(1 \times 1^2 + 1 \times 1^2)$$

$$= 1 \text{ mol/L}$$

From Equation (49)

$$\frac{1}{k} = 3.05 \times 10^{-10}(1^{-1/2})$$

$$= 3.05 \times 10^{-10} \text{ m}$$

When the pore radius is 0.3 nm (= 3 $\times 10^{-10}$ m)

$$a = 1\left[1 + \left(\frac{3}{3.05}\right)^2\right]^{-1/2} = 0.2871$$

Inserting all numerical values in Equation (1.8)

$$\frac{c_{B3}}{c_{B2}}$$
$$= \exp\left(-\frac{(6.023 \times 10^{23})(1^2)(1.602 \times 10^{-19})^2}{(8)(3.1416)(78.54)(8.854 \times 10^{-12})(8.314)(298.2)}\right)$$
$$\times \left(\frac{(1 - 0.2871)\left(\frac{78.54}{3.7}\right)}{(3 \times 10^{-10}) + (0.2871)(1.42 \times 10^{-10})\left(\frac{78.54}{3.7}\right)}\right)$$

$$= 0.00972$$

$$f' = 1 - \frac{c_{B3}}{c_{B2}} = 0.99023$$

For the rest of problems in i), problem ii) and problem iii), the answers are listed in Table 4.

The answers show the trend that:
1. When pore size increases, solute separation decreases.
2. When the solute concentration decreases, solute separation increases.
3. When the ionic valence increases, the solute separation increases.

All the above trends are experimentally observed. But the increase of solute separation by the decrease of solute concentration seems too large. Thus, the Glückauf model allows to predict the solute separation when the ionic size, ionic valence, pore size, and dielectric constant of the membrane material are known.

Future work

It is the authors' intention to present the problems and solutions for the following subjects in the future articles to be contributed to AMST.
- Membrane preparation by phase inversion
  - Solubility parameter
  - Binodal and spinodal lines
- Mixed matrix membrane
  - Prediction of membrane performance
- Pore size evaluation
- Bubble point method
- Using solute separation data
- Using AFM and SEM images
- Forward osmosis
- Nanofiltration
- Ultrafiltration and microfiltration
- Gas separation
  - Transport model
  - Series model
  - Gas separator performance
- Vapor separation
  - Transport model
- Pervaporation
  - Transport model
- Membrane distillation
  - Laplace equation for the evaluation of LEPw
  - Heat transfer
  - Mass transfer
- Membrane contactor
  - Evaluation of pore size distribution by gas flow
  - Evaluation of liquid boundary layer contribution to mass transfer, Wilson model
- Membrane extraction
  - Transport model
- Membrane adsorption
  - Adsorption isotherm and adsorption kinetics
  - Modeling for breakthrough curve
- Module calculation
  - Module performance simulation
- System calculation
  - RO system
  - Gas separation system
  - Hybrid system
- Economic analysis
  - RO economic analysis

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