

Mathematical Modelling for Separation of Binary Aqueous Solution using Hollow Fiber Reverse Osmosis Module

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Abstract—The mathematical equation for Separation of the binary aqueous solution is developed by using the Spiegler- Kedem theory. The characteristics of a B-9 hollow fibre module of Du Pont are determined by using these equations and their results are compared with the experimental results of Ohya *et al.* The agreement between these results is found to be excellent.

Keywords—Binary aqueous solution, modeling, reverse osmosis module, Spiegler-Kedem theory.

I. INTRODUCTION

IT has become essential for today's industry to comply with the environmental issues and norms for survival. The effluents from the industry consist of organic and inorganic aqueous multi-component. The separation of aqueous multi-component system has become the utmost requirements of today's scenario. Multi-component separation include production of high purity water for pharmaceutical grade, recovery of water for reuse from industrial effluents and sewage, desalination of sea water etc. In recent years, membrane separation particularly RO system has become a commercially attractive alternative to conventional unit operations for multi-component separation problems.

RO systems have applications in several areas. One of the main applications has been in water treatment for drinking water, production, desalination, food processing and waste water treatment to separation of products in bioreactors [1], [2].

Mainly four kinds of membrane module configurations are available [2]. These are spiral wound, hollow fiber, tubular and plate and frame configuration. Membranes can be made from a number of different organic and inorganic materials. The choice is based on minimizing membrane clogging and deterioration. The two major membranes module configurations used for reverse osmosis applications are spiral wound and hollow fiber. The tubular and plate and frame configurations have found good acceptance where the feed viscosity is high for example in food and dairy industry. But these modules have been less frequently used in reverse osmosis application. In the present work, a B-9 hollow-fibre module of Du Pont is studied to determine its reverse-osmosis characteristics. The analytical design equations for radial-flow hollow-fibre systems are developed by using Spiegler-Kedem

theory [3]. By these equations, the experimental data of [4] are analyzed.

II. THEORY

A. R.O. Membranes for Sea Water Desalination

The first RO membrane developed in 1960 at ULCA [3] was the asymmetric cellulose acetate membrane. Many polyamide RO membranes have been commercialized due to their high selectivity and good durability. The composite flat sheet membrane made of cross linked fully aromatic polyamide, designated as UTC-80 has been used in many actual seawater desalination plant.

For the stable operation of the plant, it is must to know the change of characteristics of the membrane with time. These characteristics can be given in the form of membrane transport parameter.

Spiegler and Kedem [2] defined the volume flux and salt flux across the membrane as follows:-

$$J_v = A(\Delta P - \sigma \Delta \pi) \quad (1)$$

$$J_s = P_m \Delta \pi + \overline{C}_s (1 - \sigma) J_v \quad (2)$$

where \overline{C}_s is the average concentration. The above equation is valid for low volume flow and low concentration gradient. For high concentration, the changing concentration profile at different flow rates has to be taken into consideration. The above equation can be transformed as

$$J_v = -P_1 [dP/dx - \sigma d\pi/dx] \quad (2)$$

$$J_s = -\overline{P} d\overline{C}_s/dx + (1 - \sigma) \overline{C}_s J_v \quad (4)$$

where P_1 is an intrinsic membrane permeability and \overline{P} is local solute permeability coefficient.

Here, $P_m = \overline{P}/2RT\Delta X$, $A = P_1/\Delta X$

The imperfection of an osmotic membrane is characterized by the "reflection" coefficient σ . When an osmotic difference, $\Delta\pi$, across and imperfectly semipermeable membrane is compensated by an applied pressure, ΔP , so that the volume flow is zero, ΔP will be smaller than $\Delta\pi$. The ratio between these two differences was defined as σ :

$$\Sigma \sigma = (\Delta P/\Delta \pi)_{J_v=0} \quad (5)$$

In an unselective membrane, where concentration gradient does not cause Volume flow at all, $\sigma = 0$. In an ideally

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semipermeable membrane, $\sigma = 1$. Thus σ is a measure of the degree of semipermeability of the membrane i.e. its ability to pass solvent in preference to solute.

$$C_{ps} = J_s / J_v \quad (6)$$

Integrating (4) by using the above equation [1,5]:

$$\begin{aligned} J_v C_{ps} &= -P dC_s/dx + (1-\sigma) \overline{C}_s J_v \\ J_v C_{ps} - (1-\sigma) C_s J_v &= -P dC_s/dx \\ J_v \int dx &= -P \int dC_s / C_{ps} - (1-\sigma) C_s J_v \\ J_v (1-\sigma) \Delta x / P &= \ln \frac{C_{ps} \sigma}{C_{ps} - C_m (1-\sigma)} \end{aligned} \quad (7)$$

Salt rejection R is defined as:

$$R = 1 - C_p / C_m \quad (8)$$

Introducing R into (7), we obtain an equation describing the salt rejection R at different flow rates J_v , as a function of flow parameter, F .

$$F = \sigma - R / \sigma (1 - R) \quad (9)$$

Where;

$$\begin{aligned} F &= e^{-J_v} (1 - \sigma) \Delta x / P \\ &= e^{-J_v} (1 - \sigma) / P_m \end{aligned} \quad (10)$$

$$\begin{aligned} F \sigma - F \sigma R &= \sigma - R \\ R - F \sigma R &= \sigma - F \sigma \\ R (1 - F \sigma) &= \sigma (1 - F) \\ R &= (1 - F) \sigma / (1 - \sigma F) = 1 - C_p / C_m \end{aligned} \quad (11)$$

At high flow rates, $F \rightarrow 0$ and hence the reflection coefficient, σ , is the limiting value of R when filtration flow overtakes diffusion.

$$J_v \rightarrow \infty; R \rightarrow \sigma$$

This fact has been used for the determination of σ , by plotting R vs. J_v or R vs. $1/J_v$ and by extrapolating $j_v \rightarrow \infty$ or $1/j_v \rightarrow 0$. But it was in the case of high or low rejected solutes that this plot became a straight line.

$$\begin{aligned} dR / dJ_v &= (dR/dF)(dF/dJ_v) = - (dR/dF) F (1 - \sigma) / P_m \\ &= - \sigma (1 - \sigma) F (dR/dF) / P_m \end{aligned} \quad (12)$$

$$\begin{aligned} \text{If } B &= 1 - \sigma / P_m \\ dR / dJ_v &= \sigma B F (1 - \sigma) / (1 - \sigma F)^2 \end{aligned} \quad (13)$$

At very low flow rates $F \rightarrow 1$, and therefore

$$\lim_{J_v \rightarrow 0} \frac{dR}{dJ_v} = \sigma / P_m \quad (14)$$

On the other hand, for high flow rates

$$\lim_{J_v \rightarrow \infty} \frac{dR}{dJ_v} = 0 \quad (15)$$

The expression of J_v can be rewritten in terms of the bulk and the permeate variables as,

$$J_v = A [(P_b - P_p) - \sigma \frac{V R g T}{M_w} \Delta C] \quad (16)$$

$$\begin{aligned} \text{where } \Delta \pi &= V R_g T C / M_w \\ \text{and } \Delta C &= C_m - C_p / C_b - C_p \end{aligned}$$

B. Concentration Polarization

There are two transport phenomena in membrane transport namely one outside and the other inside of a membrane. A solute concentration at the membrane surface (C_m) becomes higher than that of a bulk solution (C_b) due to the solute rejection nature of a membrane. This phenomenon is called "concentration Polarization". The other one is related to that inside of a membrane where solute concentration goes down from C_m to C_p , a salt concentration in the permeate [1], [5]. By taking a mass balance in the boundary layer outside of a membrane, the following equation is derived;

$$J_v C - D dC/dx = J_v C_p \quad (17)$$

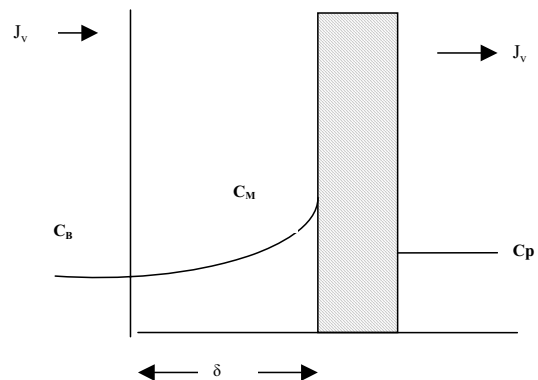


Fig. 1 Boundary Membrane Layer

Boundary conditions

$$X=0, C=C_b; X=\delta, C=C_m$$

$$D dC/dx = J_v (C - C_p)$$

$$\begin{aligned} \frac{C_m - C_p}{C_b - C_p} &= \exp \left[\frac{J_v \delta}{D} \right] \\ \ln \frac{C_m - C_p}{C_b - C_p} &= \frac{J_v \delta}{D} \\ &= \exp [J_v / K] \end{aligned} \quad (18)$$

where $K = D/\delta$

K is a mass transfer coefficient (m/s).

D = diffusivity of solute in film

S = boundary layer wall thickness

It may be expressed as a function of the Reynolds and Schmidt numbers.

$$Sh = a Re^b Sc^{1/3} \quad (19)$$

where,

Sh = Sherwood number Kd_e/D

Sc = Schmidt number $= \mu/D\rho$

Re = Reynolds number $= V_F d_e \rho/\mu$

ρ = Density of feed
 V_F = Velocity of feed
 d_e = Equivalent diameter

where a, b and c are parameters that need to be determined experimentally. There are two methods to obtain the mass-transfer coefficient from the RO experiment. One is called the Osmotic pressure method. The other one is called the velocity variation method [6].

In the former method, a high-salt rejecting membrane is used, whose σ is very close to unity. So that C_p can be ignored. The value of A is measured using pure water flux. C_m is then obtained from (1) and K is calculated from (18).

The other method is called the velocity variation method [4] which utilizes the transformed style of (18) given as follows:

$$\ln(1 - R_{obs}/R_{obs}) = \ln(1 - R/R) + J_v/K \quad (20)$$

$$\text{where, } R_{obs} = \frac{C_B - C_P}{C_B} \quad (21)$$

Once the mass transfer coefficient is determined, membrane transport parameters can be calculated from flux and rejection data taken from a RO plant, and, thus, we can trace the change in parameters with time.

The above equation can be used to estimate J_v and C_p under various conditions of ΔP , C_B and feed flow (F) when transport parameters A, σ and P_m are known. A is determined from pure water permeation experiment.

σ and P_m are determined as follows; (10) & (11) show that when J_v becomes infinity, R approaches to σ and this fact is used to determine from R values measured at different J_v (ΔP). Once σ is determined, p_m is obtained from (9) & (10). This also means that σ and P can not be determined from a single experiment and causes difficulty in knowing the changes of three transport parameters with time.

$$\text{When } \sigma \text{ is close to 1, then} \\ R = J_v / (J_v + P / \sigma) = J_v / (J_v + P_m) \quad (22)$$

So P_m is close to P, when σ is very close to 1. It is easier to determine two parameters, a and b which can be measured by a single experiment once the K value is determined. Membranes which can be used for sea water desalination usually have σ value very close to 1 for various inorganic solutes.

By combining (11), (16) and (18), we obtain:

$$C_p = \frac{C_b}{1 + \frac{\sigma}{1 - \sigma} \cdot \frac{1 - F}{\phi}} \quad (23)$$

and

$$J_v = A/p \left[(P_b - P_p) - \sigma \frac{VRgT}{Mw} \exp(J_v/k) C_b \right. \\ \left. \left(\frac{1 - F}{\exp(j_v/k)} + \frac{1 - \sigma}{\sigma} \right) \right] \quad (24)$$

C. Mass-Transfer Coefficient of RO Modules

Reference [4] derived (25) for the mass transfer coefficient of the dupont B9 permeator used in their RO experiment, ignoring the pressure drop inside the hollow fibre.

$$K = 9 * 10^{-4} V_{lm} \quad (25)$$

where K is the avg. mass transfer coefficient and V_{lm} is the logarithmic mean radial fluid velocity. Assuming that the Schmidt number in their experiment is 610 where sodium chloride solution was used, (25) may be transformed to the following dimensionless equation.

$$Sh = 0.07 Re^1 Sc^{1/3} \quad (26)$$

Reference [7] analyzed the experimental data of Toyobo 8-inch diameter modules with the friction – concentration – polarization model (FCP model/ to give:

$$Sh = 0.048 Re^{0.6} Sc^{1/3} \quad (27)$$

In their RO experiments commercial RO modules were operated with radial flow, that is cross flow perpendicular to the hollow fibres. Therefore, Reynolds and Sherwood numbers were calculated using the outer diameter of the hollow fiber as the characteristic length.

Reference [8] obtained the experimental data with the mini-fiber RO test on the basis of simplified FCP model by ignoring the shell-side solute concentration profiles of radial and axial flow directions, and the shell side mass transfer coefficients were correlated by (28).

$$Sh = 0.2 Re^{0.6} Sc^{1/3} \quad (28)$$

Here, the characteristic length in Reynolds and Sherwood numbers is not the outer diameter of the hollow fiber, but an equivalent hydraulic diameter defined as:

$$D_h = 4 (\text{cross-sectional area of flow}) / \text{wetted perimeter} \quad (29)$$

D. Equations For Pressure Drop

The pressure difference across the membrane varies throughout the membrane because of friction losses. The pressure drop for the permeate and bulk stream can be estimated using Hagen-poiseuille and the Ergun's equation respectively. These equations are given below:

Hagen-Poiseuille equation:

$$d/dz P_p = - 32\mu v_p \rho / d_i^2 \quad (30)$$

Ergun's equation:

$$d/dr P_b = - [150(1-\epsilon)^2 \mu v_r / d_p^2 \epsilon^3 + 1.75(1-\epsilon)\rho v_r^2 / d_p \epsilon^3] \quad (31)$$

Here $d_p = 6/a_v = 1.5$ do is the mean particle diameter and V_r is the superficial velocity within the module on the bulk side along the radial direction.

E. Material Balance for Binary Component

The material balance equations for both solute and solvent streams within the module are given below:

Permeate Stream

$$2 \pi r \Delta r \theta v_p \Big|_{z=z+\Delta z} - 2 \pi r \Delta r \theta v_p \Big|_{z=z} = 2 \pi r \Delta r \Delta z \zeta J_v \Big|_{z=z} \quad (31)$$

Hence,

$$d/dz v_p = J_v \zeta / \theta \quad \text{such that } v_p \Big|_{z=0} = 0, 0 \leq z \leq L \quad (32)$$

Here $\theta = d_i^2 N / D_o^2 - D_i^2$, $\zeta = 4 \theta d_o \cdot L / d_i^2 L_m$, and the length of a hollow fiber is given as:

$$L = \sqrt{L_m^2 + 4(\pi r W)^2}$$

Bulk stream solute concentration:

$$2 \pi r L v_r \Big|_{r+\Delta r} - 2 \pi r L v_r \Big|_r = - 2 \pi r \Delta r \theta v_p \quad (33)$$

Hence,

$$d/dr (r v_r) = - \theta r v_p / L \Big|_{z=L} \quad (34)$$

subject to

$$v_r \Big|_r = D_i/2 = v_F$$

Likewise for solute,

$$d/dr (r v_r C_b) = - \theta r v_p C_p / L \Big|_{z=L} \quad (35)$$

subject to $C_b \Big|_{r=D_i/2} = C_F$

For $D_i/2 \leq r \leq D_o/2$

Differentiation of (30) and subsequent substitution into equation (32) leads to:

$$d^2/dz^2 P_p = - 32 \mu \zeta J_v / d_i^2 \theta \quad \left\{ \begin{array}{l} \frac{d}{dz} P_{p/Z=0} = 0 \\ P_p = P_{atm} - l_s \cdot \frac{32 \mu}{d_i^2} v_{p/Z=L} \end{array} \right.$$

III. RESULTS AND DISCUSSION

The results of the design equations presented above were compared with the experimental data of [4]. These experimental data were obtained on a B-9 hollow-fibre module of Du Pont for an aqueous sodium chloride solution as the feed.

TABLE I
EXPERIMENTAL RESULTS OF [3] FOR AN AQUEOUS SODIUM CHLORIDE SOLUTION IN B-9 HOLLOW – FIBRE MODULE

Run	Applied pressure, atm	Feed flow rate, L/h	Feed concentration, ppm	Permeate concentration
1	26.5	596	3500	0.077
2	27.3	450	3500	0.120
3	27.5	368.8	3200	0.219
4	27.5	372.7	2775	0.184
5	23.3	368.8	3500	0.137
6	21.3	675	3500	0.077
7	21.5	602	3500	0.083
8	22.0	451	3500	0.118
9	22.3	373	3300	0.151
10	22.3	300	3100	0.242
11	17.3	471	3625	0.114

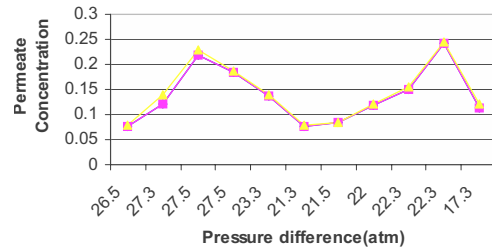


Fig. 2 Comparison of permeate concentration from numerical and experimental

SYMBOLS

- A - Hydrodynamic pure water permeability
- a - Constant used in mass transfer coefficient correlation equation
- $A[i, j]$ - Solute-solute interaction parameter of solute i and j
- b - Constant used in mass transfer coefficient correlation
- C - Concentration
- $C[i]_{\text{best}}$ - Estimated value of permeate concentration of solute i from model
- $C[i]_{\text{pexp}}$ - Experimental value of permeate concentration of solute i from model
- C_F - Feed concentration
- C_m - Concentration over the membrane surface
- C_p - Permeate concentration
- \tilde{C}_s - Logarithmic average of solute concentration on both sides of a membrane
- D - Diffusivity of solute in film
- d/dr - Derivative in radial direction
- d/dX - Derivative with respect to X
- d/dZ - Derivative in axial direction
- d_e - Equivalent diameter
- d_i - Inside fibre diameter
- D_i - Inside diameter of fibre bundle
- d_o - Outside fibre diameter
- D_o - Outside diameter of fibre bundle
- J_i - Solute i flux
- J_s - Solute flux
- J_v - Permeate flux
- J_w - Solvent flux
- K - Mass transfer coefficient
- L - Length of fibre
- P_c - Coupling coefficient
- P_m - Solute permeability
- Q_F - Feed flow rate
- Q_p - Permeate flow rate
- R - True rejection
- r - Radial coordinate
- r_i - Fibre inside radius
- R_i - Inside radius of fibre bundle
- r_o - Fibre outside radius
- V - Shell volume
- V_F - Velocity of feed
- v_F - Superficial velocity of feed at outer surface of the distributor
- W - Number of fibre wounds
- Z - Axial coordinate
- Greek Symbols
- σ - Reflection coefficient
- δ - Boundary layer film thickness
- ρ - Density of feed
- μ - Viscosity of feed
- $\Delta \Pi$ - Osmotic pressure difference across the membrane
- ε - Porosity of hollow fibre bundle

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