CHAPTER 4

MATHEMATICAL MODELS FOR NANOFILTRATION MEMBRANE

4.1 Introduction

Nanofiltration membranes are a relatively new class of membrane, which have properties in between those of ultrafiltration membranes and reverse-osmosis membranes. Their separation mechanisms involve both steric (sieving) effects and electrical (Donnan) effects. NF membranes are normally characterized in terms of the structural parameters such as pore radius and membrane thickness as well as the electrical parameters such as charge density (Bowen $et\ al.$, 1997).

The more direct technique to obtain the pore radius is by using a microscopy technique such as atomic force microscopy and the charge density by measuring the zeta potential of the membranes. In addition to being very costly, these methods usually do not provide reasonable characteristic values for nanofiltration membranes due to the limitations imposed by the nanosize pores (Bowen $et\ al.$, 1997).

One such model that has been proposed is based on the extended Nernst-Planck equation and is termed the Donnan steric pore (DSP) model (Bowen and Mohammad 1988). The model utilizes three structural and electrical parameters namely: pore radius, r_p, effective ratio of membrane thickness to porosity, $\Delta x/A_k$, and the effective charge density, X_d. These parameters can be obtained by fitting the rejection data of uncharged solutes and simple salts. In 2002 Mohammad $et\ al.$, characterized and identified the rejection mechanisms of NF membranes using extended Nernst-Planck model. For three kinds of acetone acetate NF membranes, named CA50, CA67.5 and CA86 their pore radius r_p were larger than 1.2 nm and charge density was found to be high. These results showed that the rejection mechanism depends very much on the Donnan effect rather than the steric effect. However, the membrane pore size seems to be larger than that found by Wang $et\ al.$ in 1995b and in 1997, in which the pore radii of NF membrane ranged from 0.4 to 0.8 nm.

A model to estimate structural parameters of a membrane, a pore model was developed and applied by Nakao and Kimura (1982) to the separation systems of aqueous solutions of single organic solute and ultrafiltration membrane. By

considering both steric-hindrance effect of solute and pore wall, the membrane parameters (reflection coefficient σ and solute permeability P) were interpreted. Nakao and Kimura in 1982 successfully applied the developed model to estimate r_p and $A_k/\Delta x$ of ultrafiltration membranes in terms of membrane parameters obtained from permeation experiment of different neutral solutes.

The electrical properties of membranes could be described by Teorell-Meyer-Siever (TMS) model and the Space Charge (SC) model. The TMS model assumed the uniform distribution of fixed charges in a membrane and the SC model was taken into account for the radial distributions of electrical potential and ion concentration. The SC model is more realistic than the TMS model in describing various transport phenomena of electrolytes through charge capillaries (Wang et al. 1995b). The studies of Wang et al. in 1995b and 1997 successfully applied the Steric-Hindrance Pore (SHP) model and the TMS model to estimate the membrane parameters by permeation experiments of aqueous solutions of neutral solutes (alcohols and saccharides having different molecular weight) and sodium chloride. The results showed that SPH and TMS model could be applied for NF membrane having pore size greater than 0.5 nm, especially for NF membrane used for this study (NTR 7450). Thus in our study, these models were chosen.

4.2 Basic concepts

The transport performance of NF membrane, the same as that of reverse osmosis and ultrafiltration membranes, can be described with phenomenological equations by the irreversible thermodynamic model (Kedem and Katchalsky, 1963; Katchalsky and Curran, 1965; Lakshrninayanin, 1969). This model assumes that the membrane is a black box.

Kedem and Katchalsky (1963) proposed the relation of the volume flux and the solute flux through a membrane in follow equation:

$$\begin{cases} J_v = L_p(\Delta P - \sigma.\Delta\pi) \\ J_s = P.(c_m - c_p) + (1-\sigma).J_v\overline{c} \end{cases} \tag{1}$$

where σ, P, L_p are the membrane parameters called reflection coefficient, solute permeability and pure water permeability, respectively; ΔP is the membrane pressure, $\Delta\pi$ is the osmotic pressure difference across the membrane.

For the cases of high concentration difference between the retentate and the permeate, the equation (1) can be expressed in a differential form as follows (Spiegler and Kedem 1966):

$$J_s = -P'\left(\frac{dc}{dx}\right) + (1-\sigma)J_v c \tag{2}$$

P' is the local solute permeability defined as $P'= P.\ \varDelta x$. Integrating Eq.(2) across the membrane thickness yields the rejection, R, as follows:

$$R = 1 - \frac{c_p}{c_m} = \frac{\sigma(1-F)}{(1-\sigma F)} \tag{3}$$

where

$$F = \exp\left(-\frac{1-\sigma}{P}J_v\right)$$

Equation (3) is the well-known Spiegler-Kedem equation. From Eq. (3) σ and P can be determined from experimental data of R as a function of J_v by a best-fit method. When the rejection is sufficiently high, σ can be assumed to be unity

The pure water permeability (L_p) can be obtained in experiment with pure water by fitting curve of J_v versus $\varDelta P$ with the osmotic pressure difference, $\varDelta\pi$, equal to zero. The osmotic pressure difference $\varDelta\pi$ can be determined by the concentration at the membrane surface as (Spiegler and Kedem, 1966)

$$\varDelta\pi = \pi(c_m) - \pi(c_p) = \pi(c_m) \tag{4}$$

According to the concentration polarization model, c_m can be expressed by the following equation: (Kimura and Sourirajan, 1967)

$$c_m - c_p = (c_b - c_p)\exp\left(\frac{J_v}{k}\right) \tag{5}$$

where k is the mass transfer coefficient.

The k value is generally represented as a function of the flow velocity, the equivalent hydraulic diameter of the flow channel (d_h), the diffusion coefficient of the solute (D), and the kinematic viscosity of the solution (υ). When the solution in the membrane module flows in the laminar mode, the Léveque equation can be used to calculate the k value

$$N_{Sh} = 1.62(N_{Re}.N_{Sc}.d_h/L)^{1/3} \tag{6}$$

Where, $N_{sh} = k.d_h.D$ is Sherwood number,

N_{Re}= Reynolds number= $\dfrac{u.d_h}{v}$

N_{Sc}=Schmidt number=v/D

When the permeate flux is very high (J_v/k>3), the modified mass transfer correlation equation may be used to calculate the mass transfer coefficient as follow

$$N_{Sh}=1.62(N_{Re}^{1/3}+300N_{Re-y}^{1.1})(N_{Sc}d_h/L)^{1/3} \tag{7}$$

Whereas N_{Re-y} is new Reynolds number, it can be calculated by $N_{Re-y}=\dfrac{u.d_h}{v_w}$

4.3 Determination of membrane parameters

Nanofiltration membrane weight-cut-off is about few hundreds to few thousands which is the intermediate molecular between reverse-osmosis membranes and ultrafiltration membranes. Nanofiltrations have been used to separate or concentrate organic solute. It is possible to assume that nanofiltration membranes have pore structure similar to those of ultrafiltration membranes. NF membranes consist of bundle of cylindrical capillaries with structural parameters (pore radius r_p, the ratio of membrane thickness $A_k/\Delta x$) and electrical properties, such as the surface charge density q_w (Wang et al., 1995b)

To estimate the structural parameters of membranes, the Steric-Hindrance Pore (SPH) model can be applied from permeation experimental data of aqueous solution of neutral solutes. For these, the membrane reflection, σ, and solute permeability, P, can be calculated by the following equations.

$$\sigma_{neu} = 1 - H_F S_F \tag{8}$$

$$P_{neu} = D_s H_D S_D \left(\dfrac{A_k}{\Delta x}\right) \tag{9}$$

Here H_D and H_F are called the steric-hindrance parameters related to the wall correction factors of the solute under diffusion and convection conditions, respectively, and expressed as follows:

$$\begin{cases} H_D = 1 \\ H_F = 1 + \dfrac{16}{9}\eta^2 \end{cases} \tag{10}$$

where $\eta = \dfrac{r_s}{r_p}$

η is defined as the ratio of solute radius (r_s) to pore radius (r_p). S_F and S_D are the average distribution coefficient determined only by steric effect of the solute in convection and diffusion conditions, respectively and are expressed as follows:

$$\begin{cases} S_F = (1-\eta)^2 \left[2 - (1-\eta)^2 \right] \\ S_D = (1-\eta)^2 \end{cases} \tag{11}$$

The electrical properties of membranes can be described by the Teorell-Meyer- Sievers (TMS) model. According to this model, for a system of a 1-1 type electrolyte and a NF membrane with negative charge polarity, the membrane reflection (σ) and solute permeability (P) can be expressed by the following equations:

$$\sigma_{salt} = 1 - \frac{2}{(2\alpha - 1)\xi + (\xi^2 + 4)^{1/2}} \tag{12}$$

$$P_{salt} = D_s (1 - \sigma_{salt}) \frac{A_k}{\Delta x} \tag{13}$$

where $\xi = \dfrac{X}{c}$ (14)

ξ is the ratio of the fixed charge density (X) to the electrolyte concentration (c) at membrane surface.

In the research field of interface and colloid chemistry, the electrical properties of charged membranes are usually related to the assumption of constant surface charge density (q_w) or constant of surface electrical potential (ψ_w). By assuming a NF with pore radius (r_p) and constant surface density (q_w), charge density (X) can be expressed as follows

$$X = \frac{2\pi r_p q_w}{\pi r_p^2 F} = \frac{2q_w}{r_p F} \tag{15}$$

where $q_w = \sqrt{8RT\varepsilon_r \varepsilon_0} .\sqrt{c} \sinh\left(-\frac{z_1 F \psi_w}{2RT} \right)$ (16)

with ε_r is relative dielectric constant of water (=78.303).

     ε_0 is dielectric constant of vacuum (=8.8542x10^{-12} $C^2.J^{-1}.m^{-1}$).

     z_1 is electrochemical valence of i-th ion.

     F is faraday constant (=96487 $C.mol^{-1}$).

For commercial membranes, the effective fixed charge density ϕX was introduced instead of X because of its dependence on the electrolyte concentrations. Wang et al.

1995b proposed the following equation to express the dependence of ϕX of NF membrane NTR7450 on the concentrations of 1-1 type electrolyte.

$$\phi X = \frac{71.60c^{0.5}}{1+0.01645c^{0.5}} \tag{17}$$

4.4 Diafiltration simulation

4.4.1 Concentration step

The mathematical model for diafiltration process was described by Wang *et al.* 2002 based on mass balance of any component passed through the membrane.

Let A (m^2) is the total filtration area and V_f (m^3) is volume of feed solution, the mass balance for component i in feed solution gives in the following equation:

$$\frac{d(V_f c_{f,i})}{dt} = -J_v A c_{p,i}$$

$$\text{or } V_f \frac{dc_{f,i}}{dt} + c_{f,i}\frac{dV_f}{dt} = -J_v A c_{p,i} \tag{18}$$

Whereas $c_{f,i}$ and $c_{p,i}$ are feed and permeate concentration of i respectively. J_V is volume flux.

For concentration step, the volume rate feed solution always gives as

$$\frac{dV_f}{dt} = -J_v A \tag{19}$$

By substitution of Eq. (19) into Eq. (18) gives us

$$\frac{d\ln(c_{f,i})}{dt} = \left(\frac{c_{p,i}}{c_{f,i}} - 1\right)\frac{d\ln(V_f)}{dt} \tag{20}$$

The observed rejection of i is defined as

$$R_{obs,i} = 1 - \frac{c_{p,i}}{c_{f,i}} \tag{21}$$

so Eq. (20) can be rewritten as follow

$$\frac{d\ln(c_{f,i})}{dt} = -R_{obs,i}\frac{d\ln(V_f)}{dt}$$

It is more convenient to consider the observed rejection as constant, so Eq. (20) can be expressed in the dimensionless form