

# The development of predictive modeling of nanofiltration membrane properties : A review

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## Abstract

Nanofiltration (NF) membranes, a relatively recent type of membranes, possess properties in between those of ultrafiltration (UF) and reverse osmosis (RO). The ionic transport mechanisms are therefore governed by both of steric and charge effects. This combined effect offers a value added to the membrane separation abilities, which covers almost all range of liquid-liquid separation system. For all type of unit operation such as membrane separation system, having a good predictive tool is certainly vital in process performance prediction, hence, process design and optimization. In NF separation system, however, the understanding of ionic transport mechanisms have not been fully understood. The previously developed predictive models have been revised and modified by other researchers intermittently. Two main approaches have been used thus far to model the transport of ionic species through NF membranes. One approach is through the Spiegler-Kedem model (Schirg and Widmer, 1992; Leveinstein et al., 1996). This black box approach allows the membrane to be characterized in terms of salt permeability ( $P_s$ ) and reflection coefficient ( $\sigma$ ). The second approach describes the transport of ions in terms of an effective membrane thickness/porosity  $\Delta x/A_k$ , effective pore radius,  $r_p$ , and effective membrane charge density,  $X_d$ . This paper reviews these two approaches including the assumptions used in model derivation, descriptions of mathematical formulation, descriptions of transport mechanisms and membrane pore size and effective charge density quantification. The weakness and strength of the two approaches are also highlighted. Of these two approaches, researchers were found to be more interested in applying model that was based on the extended Nernst-Planck equation. This was due to its ability to describe and illustrate the ionic transport mechanisms comprehensively and in more detail.

**Keywords** : Review, NF models, spiegler-kedem, extended nernst-planck

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## 1. Introduction

Nanofiltration (NF) membranes, a relatively recent type of membranes, possess properties in between those of ultrafiltration (UF) and reverse osmosis (RO). This promising technique has attracted increasing attention over recent years due to the development of new applications in several areas such as textile industry (removal of dye

from waste rinse water), paper and plating industries (limiting of the consumption of clean water by recycling waste water), drinking water production and etc.

At fundamental level, NF process is complex. The ionic transport mechanisms are governed by both of steric and charge effects. Steric effect is caused by the difference of sizes between membranes pores and solutes while Donnan effect is actually a result of charge polarities between membranes and solutes. This combined effects offers a value added to the membrane separation abilities, which covers almost all range of liquid-liquid separation system. For all type of unit operation such as membrane separation system, having a good predictive tools is certainly vital in process performance prediction, hence, process design and optimization. In NF separation system, however, the understanding of ionic transport mechanisms have not been yet fully understood, the previously developed predictive model have been revised and toted up by other researches intermittently.

This review will include the chronology of predictive models development which is important to convey a fundamental understanding and simple quantification of governing phenomena in a way that has the potential for industrial application. In addition, this review will cover the discussion on weakness and strength of the developed models approach in an attempt to highlight the most accurate and practical model. As a result, adapted model will assist in determining the most convenient transport mechanisms through the NF membranes.

## **2. Chronology of predictive models development for nanofiltration membranes separation.**

Basically, there are two approaches in membrane characterization. They are direct measurement method and analytical method. The analytical method involves fittings of solute rejection data with the mathematical model and most researchers have a preference to this method rather than the first one. This is because, NF membranes are developed in nanometer scale and almost none of the current analysis techniques can conveniently and accurately characterized the membrane. In the second method, flux and solute rejection data are corresponded to the structure parameter such as pore size, pore size distribution, thickness and charge capacity by using mathematical models that have been developed based on the solutes transport mechanisms through the porous membrane.

Since 1980's, a lot of works have been devoted to develop reliable mathematical models in characterizing the structure of nanofiltration membranes. There have been two approaches used in analyzing the transport mechanisms through a membrane. The first approach is based on the irreversible thermodynamics derived by Kedem and Katchalsky (1958) and Spiegler and Kedem (1966). The second approach was introduced by Ferry (Ferry, 1936) and known as the hydrodynamics model or pore model.

## 2.1. First approach : spiegler and kedem (1966)

In the first approach, the membrane is treated as a black box by neglecting the porosity of the membrane. Therefore, detail information about the solute transport mechanisms can not be obtained. The characterization is conducted by considering three transport mechanisms i.e; hydraulic permeability ( $P_m$ ), solute permeability ( $P_s$ ) and reflection coefficient ( $\sigma$ ). Volume flux and solute flux are dependent on the driving force which is the operating pressure and osmotic pressure. Kedem and Katchalsky (1958) expressed the volume flux and solute flux across the membrane as :-

$$J_v = -P_m(\Delta P - \sigma\Delta\pi) \quad (2.1)$$

$$j_s = -P_s \frac{dc_s}{dx} + (1 - \sigma)c_s J_v \quad (2.2)$$

where  $J_v$  is the volume flux ( $\text{ms}^{-1}$ ),  $j_s$  is the solute flux ( $\text{mols}^{-1}\text{m}^{-2}$ ),  $P_m$  is the pure water permeability ( $\text{ms}^{-1}\text{bar}^{-1}$ ),  $\Delta P$  is the transmembrane pressure (bar),  $\Delta\pi$  is the osmotic pressure difference across the membrane (bar),  $c_s$  is the logarithm averaged concentration of solute,  $dc_s/dx$  is the concentration gradient across the membrane ( $\text{molm}^{-3}$ ),  $\sigma$  is the reflection coefficient and  $P_s$  is the permeability of solute ( $\text{ms}^{-1}$ ).

Integration of equation (2.2) will give the expression for solute rejection. This equation is known as Spiegler-Kedem equation:-

$$R_{sebenar} = 1 - \frac{(1 - \sigma)}{(1 - \sigma F)} = 1 - \frac{C_p}{C_m} \quad (2.3)$$

where

$$F = \exp(1 - J_v(1 - \sigma)/P_s) \quad (2.4)$$

$R_{real}$  is the actual rejection value which consider the concentration polarization factor while  $C_p$  and  $C_m$  is respectively the feed concentration of solute and permeate. From this equation, it shows that as the flux,  $J_v$  is approaching infinity, the rejection,  $R$  will move towards  $\sigma$ . Transport parameter, water permeability,  $P_m$  is evaluated using equation (2.1), by assuming that the osmotic pressure difference is zero. Logarithm averaged concentration,  $c_{lm}$  is used to determine  $\sigma$  and  $P_s$ . Equation (2.2) can be written as :-

$$\frac{j_s}{\Delta c} = P + (1 - \sigma)(J_v c_{lm} / \Delta c) \quad (2.5)$$

where  $\Delta c = C_m - C_p$ . If the correlation between  $j_s/\Delta c$  and  $J_v c_{lm}/\Delta c$  is linear, the  $\sigma$  dan  $P_s$  parameter will be the slope and the intersection of y-axis. In equation (2.4) and (2.5), as  $J_v \rightarrow 0$  (high flux),  $R \rightarrow \sigma$ . This means that the rejection,  $R$  will increase with the increment of volume flux until the maximum value,  $\sigma$  is achieved. The rate where the maximum value  $\sigma$  is reached, depends on the solute permeability,  $P_s$ . When the  $P_s$  is low, the rejection will drastically increase with the flux,  $J_v$  increment. As a result,  $\sigma$  and  $R$  depends on the  $J_v$  value and the pressure difference.

$P_m$ ,  $\sigma$  and  $P_s$  parameters are analyzed using pore theory in order to understand the actual structure of a membrane. Pappenheimer (1951) had leded the pore theory development to analyze the transcapillary transport. In this theory, he explained that solute flux consists of permeate flow and diffusion. Both of these flows are interfered by steric hindrance factor and friction force at the feed point of the membrane pore. Verniory et al. (1973) modified the pore theory in order to fix with the Haberman and Sayre (1958) correction factor and irreversible thermodynamic theory (Kedem and Katchalsky, 1958) to predict the membrane structure. Equation of solute flux is expressed as follows;

$$j_s = Df(q)S_D \frac{A_k}{\Delta x} (C_m - C_p) + J_v c g(q) S_F \quad (2.6)$$

Where  $A_k$  is the ratio of pore cross sectional area over effective cross sectional area of the membrane.  $S_D$  and  $S_F$  is the steric hindrance factor which respectively for diffusion and filtrate.  $S_D$  and  $S_F$  can be defined as:-

$$S_D = (1 - q)^2 \quad (2.7)$$

$$S_F = 2(1 - q)^2 - (1 - q)^4 \quad (2.8)$$

where  $q$  is the ratio of stokes radius over pore radius,  $q = r_s/r_p$ . Meanwhile  $f(q)$  and  $g(q)$  are the correction factors for concentration effect on the membrane wall. Haberman and Sayre (1958) evalute  $f(q)$  and  $g(q)$  as the following equation:-

$$f(q) = (1 - 2.1q + 2.1q^3 - 1.79q^6) / (1 - 0.76q^5) \quad (2.9)$$

$$g(q) = \{1 - \frac{2}{3}q^2 - 0.2q^5\} / (1 - 0.76q^5) \quad (2.10)$$

Comparing the equation (2.6) and (2.2), transport parameters,  $\sigma$  dan  $P_s$  can be related to structure parameter of the membrane which is the pore radius,  $r_p$  and ratio of membrane effective thickness to porosity,  $\Delta x/A_k$ .

$$\sigma = 1 - g(q)S_F \quad (2.11)$$

$$P_s = Df(q)S_D (\Delta x / A_k) \quad (2.12)$$

As a charges membrane is placed in an electrolyte solution, ion equilibrium will exist between membrane and solution so as to maintain the electroneutrality. Since there is constant charged capacity in the membrane, charged ion concentration in the membrane become imbalance to the charge concentration in bulk solution. Counter-ion concentration (ion with opposite charge to the membrane) is higher in membrane phase compare to the concentration in bulk solution, in the meantime concentration of co-ion is relatively lower in membrane phase. Potential gradient which exists on the interface is known as Donnan potential. Donnan potential occurs in order to balance the counter-ion transport into the solution phase and co-ion into the membrane phase. As a result, in charged solute system, ion rejection takes place due to Donnan equilibrium effect. One of the major factors influences on ion rejection is the ion concentration.

Jitsuvara and Kimura (1983) recommended the application of Spiegler-Kedem model for analyzing rejection of single salt solution data by charged membrane. Concentration of solutes in the membrane was related to the solution concentration through Donnan equilibrium equation. Effect of effective charge density was determined by using equation that relates the activity coefficient and membrane charge. They reported that ion rejection decreased as the concentration of salt solution increased. By using the equation (2.3), they discovered that increment in salt concentration could cause an improvement in salt permeability,  $P_s$  value and decrement in reflection coefficient value,  $\sigma$ . Schirg and Widmer (1992) measured the salt rejection data using NF membranes for binary NaCl-H<sub>2</sub>O and tertiary NaCl-H<sub>2</sub>O-colouring systems. They also include the correction factor for concentration polarization. Real rejection equation is expressed as (Schirg dan Widmer, 1992) :-

$$R_{real} = \left[ 1 + \frac{1 - R_{observed}}{R_{observed}} \exp\left[-\frac{J_v}{D} \delta\right] \right]^{-1} \quad (2.13)$$

where  $D$  is the permeability coefficient and  $\delta$ , is the thin film thickness. Application of this approach in characterization of membrane is relatively less. Most of the researchers tend to adapt those model approaches that based on extended Nernst-Planck equation because the description is more comprehensive and detail.

## 2.2. Second approach : hydrodynamic approach or pore model

In the hydrodynamic approach or extended Nernst-Planck equation based model, a membrane is assumed to consist of discrete pores which allow the transport of solute across its barrier. Ferry (1936), the founder of this model used the structure parameter such as pore size, thickness and tortuosity to describe the mechanisms of solute transport. Hydrodynamic principle has been applied in order to visualize the transport of spherical solute through capillary in the membrane. The basic equation in pore model development is based on the extended Nernst-Planck equation.

## 3. Extended nernst-planck equation

This equation was introduced by Schlogl (1966) and Dresner (1972) and it is applicable to describe the behavior of separation process by NF membrane. This equation covers all of the three significant aspects in transport mechanisms such as diffusion, electromigration and convection.

In order to explain the pore model based on the extended Nernst-Planck equation, several assumptions have been made such as;

- i) Solution is assumed to be ideal.
- ii) Charge capacity is uniform in any point within the separation zone in the membrane.
- iii) All ions exist in the membrane are transportable.

- iv) Donnan equilibrium takes place in the interface between membrane and outer solution.

The extended Nernst-Planck equation (Schlogyl 1966 dan Dresner dan Johnson, 1972) is:-

$$j_i = -c_i D_{i,p} \left( \frac{d}{dx} \bar{\mu}_i \right) + K_{i,c} c_i J_v \quad (2.14)$$

where  $j_i$  is the flux for ion- $i$ .  $D_{i,p}$  is the bulk permeability of ion- $i$ ,  $K_{i,d}$  and  $K_{i,c}$  is respectively the diffusion and convection hindrance factors,  $\bar{\mu}_i$  is the electrochemical potential of ion- $i$ .  $\bar{\mu}_i$ , can be expressed as:-

$$\bar{\mu}_i = R_g T \ln a_i + V_{si} P + z_i F \phi + p_{emalar} \quad (2.15)$$

where  $R_g$  is the gas constant,  $T$ , absolute temperature (298K),  $V_{si}$ , specific volume of ion- $i$ ,  $P$  operating pressure,  $z_i$ , valence of ion- $i$ ;  $F$ , Faraday constant (96487 Cmol<sup>-1</sup>);  $a_i$ , activity coefficient of ion- $i$  dan  $\phi$ , electrical potential in the membrane. Substituting the equation (2.14) into (2.15), this equation will be derived:-

$$j_i = -c_i D_{i,p} \frac{d}{dx} \ln a_i - \frac{z_i c_i D_{i,p}}{RT} F \frac{d\phi}{dx} - \frac{c_i D_{i,p}}{RT} V_{si} \frac{dP}{dx} + K_{i,c} c_i J_v \quad (2.16)$$

The third expression on the left-hand of the equation is equal to zero, which applicable for low pressure case, pressure effect is neglected. (Dickson, 1988; Burghoff et al., 1988). Therefore  $dP/dx$  is zero.

$$j_i = -c_i D_{i,p} \frac{d}{dx} \ln a_i - \frac{z_i c_i D_{i,p}}{RT} F \frac{d\phi}{dx} + K_{i,c} c_i J_v \quad (2.17)$$

Activity coefficient,  $a_i$  is expressed as  $a_i = c_i \gamma_i$ , where  $a_i$  is the activity coefficient for solute in the capillary. By substituting  $d \ln a_i = \frac{d a_i}{a}$ , the equation (2.17) will be:

$$j_i = -\frac{D_{i,p}}{\gamma_i} \frac{d(c_i \gamma_i)}{dx} - \frac{z_i c_i D_{i,p}}{RT} F \frac{d\phi}{dx} + K_{i,c} c_i J_v \quad (2.18)$$

Simplify the integration of  $\frac{d(c_i \gamma_i)}{dx}$ , so

$$j_i = -c_i D_{i,p} \left( \frac{d \ln \gamma_i}{\gamma_i} \right) - D_{i,p} \frac{dc_i}{dx} - \frac{z_i c_i D_{i,p}}{RT} F \frac{d\phi}{dx} + K_{i,c} c_i J_v \quad (2.19)$$

And,  $\frac{d \ln \gamma_i}{\gamma_i}$  is neglected (Schogyl 1966), extended Nernst-Planck equation is finally simplified to:-

$$j_i = -D_{i,p} \frac{dc_i}{dx} - \frac{z_i c_i D_{i,p}}{RT} F \frac{d\phi}{dx} + K_{i,c} c_i J_v \quad (2.20)$$

Obviously, the three expressions on the left-hand of the equation represent the transport mechanisms which are diffusion, electromigration, and convection.

#### **4. Development of models based on the extended nernst-planck equation**

A detail descriptive of mathematical models development will be done by using negatively charged membrane and two types of electrolyte systems i.e; uncharged solutes system and charged solutes system. Pore information such as radius, size and porosity distribution is obtained from fitting of neutral solutes rejection data. Based on this information, fitting of charged rejection data is eventually used to determine the effective charge capacity,  $X_d$ . Uncharged solutes system refers to neutrally charged solution such as glucose, vitamin, glycerin, sucrose, rafinos and etc. This solution is free of any anion or cation. Meanwhile, charged electrolyte system is in form of salt solution which contains anion and cation. The existence of both of these ions will cause the Donnan effect and consequently affect the separation performance together with the steric effect.

Several models have been developed based on the extended Nernst-Planck equation. Steric and Donnan effects have been manipulated in different conditions and assumptions. Nakao and Kimura (1982) introduced a model called steric hindrance pore, SHP. Basically, this model started with irreversible thermodynamic principle, which assumes a membrane as a black box. As a result, the detailed transport mechanisms of solute can not be obtained.

Then, Tsuru et al. (1991a, 1991b) has derived a model to predict the ion rejection in charged RO membranes for binary and tertiary systems. The extended Nernst-Planck equation was combined with constant charge model (introduced by Teorell (1951) and Meyer and Sievers (1936)). This model was then known as Teorell-Meyer Sievers, model or TMS. The main assumption made during the development of this model is; constant charge in the membrane is distributed uniformly. The separation behavior only considers the electrostatic effect but not the steric effect. Thus, the size of ion is assumed to be smaller than the membrane pore size. However, many difficulties arise since the constant charge distribution can not be simply obtained. Furthermore, information on constant charge distribution pattern in the membrane and ion migration polar is complicated to be obtained physically.

Wang et al. (1995a) recommended the space charge model, SCPM. This model assumes that a membrane consists of a bind of capillaries with charged surface. Differ from TMS model, SCPM model assumes that the membrane possesses a radial electrical potential and concentration distributions. The ions however are assumed as charges i.e. no steric effects due to the ions sizes.

In order to combine both steric and Donnan effects, Deen, et al., (1980) and Wang et al. (1995c, 1997) devoted their studies to develop a model of electrostatic and steric-hindrance, ES.ES model is a combination of SHP and SCPM model and it apply both

electrostatic and steric effects to describe the behavior of solute separation through the membrane. Assumption made by Wang et al., (1995c) are:-

- i) Membrane is assumed to consist of a bunch of capillary with pore radius  $r_p$ , ratio of membrane surface porosity to membrane thickness,  $Ak/\Delta x$  and surface charge density,  $q_w$  and negatively charged membrane.
- ii) Organic electrolyte is distributed completely into large ion and small ion.
- iii) Steric hindrance effect is only considered for large ion (Stokes radius,  $r_s$  is evaluated from Stokes-Einstein)
- iv) Ion concentration distribution in the membrane capillary obey the Poisson-Boltzmann or Donnan equilibrium (Wang et al., 1995).
- v) Ion flux and pure water velocity (as solvent) phenomenon in membrane capillary is respectively represented by the extended Nernst-Planck equation and Hagen-Poiseuille (Wang et al, 1995a).
- vi) For ternary system which is water/inorganic electrolyte/organic electrolytes, the contribution of organic solution toward the radial and axial electrical potential distribution is assumed negligible.

In this investigation Wang et al., (1995c) has successfully proven that the rejection of neutral solute is only affected by steric hindrance factors.

As a result of improvement and modification processes to ES model, two most recent models have been derived. Both models are hybrid model (HM) and DSPM model. The HM model assumes that a membrane is homogen while the DSPM model assumes that a membrane is porous. This is the major difference between these two models and such assumptions will convey a different definition in terms of flux, concentration, potential and ion hindrance factors.

The development of these two model was started with the extended Nernst-Planck equation which can be expressed as:-

$$j_i = -K_{i,d}D_{i,\infty} \frac{dc_i^m}{dx} - \frac{z_i c_i^m K_{i,d} D_i}{RT} F \frac{d\psi^m}{dx} + K_{i,c} c_i^m J_v \quad (2.40)$$

$D_{i,p}$  is the diffusivity of ion-i and  $k_{i,c}$  is the hindrance factor for convection.  $D_{i,p}$  can be written as:-

$$D_{i,p} = k_{i,d} D_{i,\infty} \quad (2.41)$$

where  $K_{i,d}$  is the hindrance factor for diffusion and  $D_{i,\infty}$  is the diffusivity of ion-i in the bulk solution. Each solute that moves in a solution will experience the electrostatic force caused by the solvent. When the solute moves inside a narrow space like the membrane pores, the electrostatic effect becoming more significant.  $K_{i,d}$  and  $K_{i,c}$  are functions of  $\lambda$ , which is the ratio of ionic to pore radius of the membrane. Moreover, Bowen and Sharif (1994) also relates the parameters  $K_{i,d}$  and  $K_{i,c}$  to the hydrodynamic properties of solute, which is assumed to be of spherical shape and moving inside a long cylindrical capillary in the membrane. The hydrodynamic parameters are hydrodynamic coefficient ( $K^{-1}$ ), enhance drag and  $G$ , lag coefficient. They have solved the governing equations using the



finite element method to determine  $K^{-1}$  and  $G$  for  $\lambda$  in the range of 0 to 0.95. Thus, for  $0 < \lambda < 0.95$ , values of  $K^{-1}$  and  $G$  can be evaluated as:-

$$K^{-1}(\lambda, 0) = 1.0 - 2.30\lambda + 1.154\lambda^2 + 0.22\lambda^3 \quad (2.42)$$

$$G(\lambda, 0) = 1.0 + 0.054\lambda - 0.988\lambda^2 + 0.441\lambda^3 \quad (2.43)$$

Bowen dan Mukhtar (1996) recommended that hindrance factor for diffusion is expressed as:-

$$K_{i,d} = D_{i,p} / D_{i,\infty} \quad (2.44)$$

where  $D_{i,p}$  is the hindered diffusivity of ion- $i$  in pore. Hindrance factor for convection is defined as:-

$$K_{i,c} = \mu_s / \mu_x \quad (2.45)$$

where  $\mu_s$  is the velocity of the solvent and  $\mu_x$  is the maximum velocity of solute in pore. For  $0 < \lambda < 0.4$ , relationship between  $K_{i,d}$  and  $K_{i,c}$  and  $\lambda$  is given as:-

$$K_{i,d} = -1.705\lambda + 0.946 \quad (2.46)$$

$$K_{i,c} = -0.301\lambda + 1.022 \quad (2.47)$$

Based on the above functions, it is obviously showed that correction factor for diffusion is higher than those of convection. Information on ionic radius and pore radius are necessary for calculation of  $K_{i,d}$  and  $K_{i,c}$ . Diffusivity of ion- $i$  in bulk solution,  $D_{i,\infty}$  can be related to its mobility,  $\mu_i^0$  using Fick's law of diffusion (Moore 1972) and given as:-

$$D_{i,\infty} = \frac{k_B T \mu_i^0}{Q_i} \quad (2.48)$$

where  $Q_i = |ze_i|$  is the charge of ion- $i$ .  $e$  is the electron constant ( $1.602 \times 10^{-19}$  C) and  $z_i$  is the valence of ion  $i$ .  $K_B$  is the Boltzmann constant ( $1.38062 \times 10^{-23}$  JK<sup>-1</sup>), and  $T$  is the operating temperature (K). The value of mobility for ion- $i$  can be obtained from any physical data tables of organic or inorganic matter. Substituting all constants in equation (2.48), the equation can be simplified to:-

$$D_{i,\infty} = \frac{2.568 \times 10^{-2} \mu_i^0}{|z_i|} \quad (2.49)$$

The ionic radius is related to diffusivity through the Stokes-Einstein equation which defined as:-

$$D_{i,\infty} = \frac{k_B T}{6\pi\mu r_{s,i}} \quad (2.50)$$

By substituting the constants value and  $\mu$ , the fluid concentration is assumed to be the concentration of water at 25°C which is  $8.9 \times 10^{-4} \text{ kgm}^{-1}\text{s}^{-1}$ , the equation for determining solute radius can be expressed as

$$r_{s,i} = \frac{9.550 \times 10^{-18} |z_i|}{\mu_i^o} \quad (2.51)$$

In transport of ion- $i$  through the membrane, the system must maintain the electroneutrality. The electroneutrality in the bulk solution is given as:-

$$\sum_{i=1}^n z_i c_i^o = 0 \quad \text{in bulk solution} \quad (2.52)$$

$$\sum_{i=1}^n z_i c_i = -X \quad \text{in membrane} \quad (2.53)$$

where  $c_i^o$  is the bulk concentration of ion  $i$ ,  $c_i$  is the concentration of ion- $i$  in the membrane,  $X$  is the effective volumetric charge density and is assumed to be constant at all points in the active part of the membrane. The zero current condition inside the membrane is expressed as:-

$$I_c = \sum_{i=1}^n F(z_i j_i) = 0 \quad (2.54)$$

By rearranging the equation (2.54), the concentration gradient and potential gradient is written as :-

$$\frac{dc_i}{dx} = \frac{J_v}{D_{i,p}} (K_{i,c} c_i - C_{i,p}) - \frac{z_i c_i}{RT} F \frac{d\phi}{dx} \quad (2.55)$$

$$\text{where } j_i = J_v C_{i,p} \quad (2.56)$$

$$\frac{d\phi}{dx} = \frac{\sum_{i=1}^n \frac{z_i J_v}{D_{i,p}} (K_{i,c} c_i - C_{i,p})}{\frac{F}{RT} \sum_{i=1}^n (z_i c_i)} \quad (2.57)$$

Equation (2.55) and (2.57) can be solved by using the following boundary conditions together with the equation for electroneutrality.

$$\text{At } x = 0, \quad C_i = C_{i,w}; \quad (2.58)$$

$$\text{At } x = \Delta x, \quad C_i = C_{i,p} \quad (2.59)$$

Where  $C_{i,w}$  and  $C_{i,p}$  are the feed and permeate concentration of ion-I at the interface of the membrane respectively. These are the concentration of ion- $i$  just outside the membrane. In order to determine the concentration of ion-I just inside the membrane, the extended Nernst-Planck equation is combined with the Donnan equilibrium condition and thus giving this following equation:-

$$\frac{\gamma_i c_i}{\gamma_i^o C_i^o} = \phi \exp - \frac{z_i F}{RT} \Delta \phi_D \quad (2.60)$$

where

$$\phi = (1 - \lambda)^2 \quad (2.61)$$

The steric partitioning term  $\phi$ , in the Donnan equilibrium equation is accounted for the steric effect at the entrance to the membrane.

Based on a comparison done by Bowen & Mohammad (1998a) using salt solution and uncharged solute, the finding shows those NF membranes is porous and not as being described by HM model. This fact is supported by direct observation result using Atomic Force Microscope (AFM), which shows the discrete pores exist in nanometer dimension. Based on this finding, DSPM model has been identified as the most appropriate and accurate predictive model for characterization of NF membranes separation process. In addition, this model is developed based on the extended Nernst-Planck equation that consider all of the transport mechanisms i.e; diffusion, electromigration and convection.

## 5. DSPM model

The derivation of DSPM model has been summarized and the important equations involve in this model are shown below;

Potential Gradient

$$\frac{d\phi}{dx} = \frac{\sum_{i=1}^n \frac{z_i J_v}{D_{i,p}} (K_{i,c} c_i - C_{i,p})}{\frac{F}{RT} \sum_{i=1}^n (z_i c_i)} \quad (4.1)$$

where  $J_v$  is the volume flux,  $z_i$ , ion valence,  $D_{i,p}$  the permeability of ion- $i$ ,  $K_{i,c}$  convection hindrance factor,  $c_i$  and  $C_{i,p}$  is concentration of ion- $i$  in the membrane and in permeate respectively.

Concentration gradients,

$$\frac{dc_i}{dx} = \frac{J_v}{D_{i,p}}(K_{i,c}c_i - C_{i,p}) - \frac{z_i c_i}{RT} F \frac{d\phi}{dx} \quad (4.2)$$

Donnan equilibrium equation,

$$\frac{c_i}{C_{i,w}} = \phi \exp - \frac{z_i F}{RT} \Delta\phi_D \quad (4.3)$$

$$\text{and } \phi = (1 - \lambda)^2 \quad (4.4)$$

where  $\phi$  is the steric effect and  $\lambda$  is the ratio of stokes radius to membrane pore radius ( $\lambda = r_s/r_p$ ). Electroneutrality equations:-

➤ In feed , 
$$\sum_{i=1}^n z_i C_{i,w} = 0 \quad (4.5)$$

➤ In membrane, 
$$\sum_{i=1}^n z_i c_i = -X_d \quad (4.6)$$

➤ In permeate, 
$$\sum_{i=1}^n z_i C_{i,p} = 0 \quad (4.7)$$

## 6. Conclusion

Membrane characterization is becoming more important not only for the membrane users or membrane manufacturers but also for the membrane technologist. The characterization methods are very useful in order to understand the membrane pore structure such as pore radius, pore density, pore shape and etc. Such information is needed for selection of an appropriate membrane specific application, determining the membrane casting conditions, controlling the membrane quality and understanding and predicting separation performance for various substances. For that purpose, useful predictive models are certainly vital in process performance prediction, hence, process design and optimization. In predictive model development, the model derivation is basically based on two approaches; the irreversible thermodynamic approach and the hydrodynamic approach. Both of these approaches have been used in order to determine the ion transport mechanisms during separation process which is commonly governed by both of steric and charge effects. Of these two approaches researchers are found to be more interested in applying such model that based on the extended Nernst-Planck equation or hydrodynamic approach due to its description illustration of ionic transport mechanisms is more comprehensive and detail. This approach includes the three ion transport mechanisms in membrane separation which are diffusion, electromigration and convection.

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