Chapter 6 : Modelling - Surface Force Pore-Flow Model

6.1 Introduction

Reverse osmosis is a process to separate solute and solvent components in the solution. Although the solvent is usually water, it is not necessarily restricted to water. The pore radius of membrane is less than 1 nanometer (nm). While solvent water molecules, whose radius is about one tenth of 1 nm, can pass through the membrane freely, electrolyte solutes, such as sodium chloride and organic solutes that contain more than one hydrophilic functional group in the molecule, cannot pass through the membrane. These solutes are either rejected from the membrane surface, or they are more strongly attracted to the solvent water phase than to the membrane surface. In this study, reverse osmosis has been employed to ensure very high quality of the reclaimed water for process use.

Reverse osmosis process has been discussed extensively on the basis of preferential sorption-capillary flow mechanism (Sourirajan, 1970, 1978; Sourirajan and Matsuura, 1977). These mechanisms explain the negative or positive adsorption of solute at membrane-solution interface and fluid

permeation through the pores. Apart from these interactions, the pore size distribution also plays an important role in membrane based separation processes. The surface of a membrane contains microscopic pores through which a fluid is transported under pressure. Here, the structure and dimension of pores are important since it affects the friction factor and flow characteristics of the membrane separation. The geometrical structure of the pores and the interactions among solute, solvent and pore-wall are explained in the surface force pore-flow (SFPF) model proposed by Matsuura and Sourirajan (1981). The surface force acting on the solutes is described by an electrostatic or a Lennard-Jones type potential function. This analysis provides general expression for solute separation which applies to both negative and positive adsorption of solutes.

The pore size and its distribution have been a major aspect of research in membrane filtration since the early stage of its development. Various physical methods were used to correlate pressure drop and flow rate as a function of pore diameter using Poiseuille's and Newton's law. The average pore size was determined using bubble pressure methods. Apart from these, porosimetric analysis by mercury intrusion in the pores, gas permeability test, studies based on electron microscope and thermoporometry were used to determine the pore size distribution. However, a more reliable technique to determine the

distribution of fine pores is based on the permeation of the solute molecules of known size (Chan et al., 1984).

Various other techniques have been used to determine the pore size distribution in a membrane. These include adsorption of gases such as CO_2 and N_2 (Bhattacharya, 1986) and liquid chromotography and filtration data correlated to pore size (Chan, et al., 1982). The results indicate that a normal or a log-normal distribution of pore sizes is a good assumption in most cases. Chan et al. (1984) employed two normal distributions to account for bimodal distribution with two distinct peaks in pore size in some cases and also a uniform distribution of pores to estimate separation efficiency of ethyl t-butyl ether and sucrose.

The existence of pore size distribution in any porous membrane makes the system amenable to stochastic analysis. In this work, Monte Carlo technique has been adopted to forecast the separation efficiency of a membrane under a given circumstances. It has been shown that separation efficiency matches very well with the experimental results in this study which involved the cellulose acetate/ sodium chloride/ water system. The results have been compared with the separation factor for sodium chloride - water system using the SFPF model. In this work it has been shown that Monte Carlo simulation has some advantages over the numerical integration scheme for the Gaussian pore size distribution as

suggested by Matsuura (1994). These include the determination of the effect of separation efficiency on pores outside the 3σ limits. Moreover the average separation efficiency can be determined based on the average area or the diameter of the pores. It is also possible to take into account non-circular pore geometry into account.

6.2 The Simulation Scheme

The present simulation scheme employs a Monte Carlo technique based on the SFPF model of Matsuura and Sourirajan (1981). This works on the principle of random pore size generation from a known mean and standard deviation and applying the SFPF model to estimate the separation efficiency of each pore. The mean separation efficiency is determined by averaging the individual separation efficiencies based on either area or diameter. The basic equations to determine the separation factor of a solute are given here.

The concentration of solute in the feed and at the membrane surface are different due to concentration polarisation phenomena. As a result, two different solute separation functions are obtained. These are given by equations (1) and (2) as follows:

$$f = (c_{A1} - c_{A3}) / c_{A1} \quad \text{..... (1)}$$

$$f' = (c_{A2} - c_{A3}) / c_{A1} \quad \text{..... (2)}$$

The dimensionless solute concentration at the pore outlet C_A is defined by the following equation :

$$C_A = c_{A3} / c_{A2} \quad \text{..... (3)}$$

In equation (1) and (2), f and f ' are defined as solute separation based on the solute concentration in the bulk feed and true value of solute separation by the membrane pore. The concentration of the solute in the feed, at the membrane/solution boundary and at the outlet are given by c_{A1}, c_{A2} and c_{A3} respectively. The relationship between f and f ' is as follows:

$$f = f' / (f' + [(1 - f') \exp(v_s/k)]) \quad \text{..... (4)}$$

where v_s and k are the permeation velocity (m/s) and the mass transfer coefficient (m/s) of the solute in the boundary region (Matsuura, 1994).

The factor f ' is expressed by the following equation in the SFPF model :

$$f' = 1 - {}_0\int^1 \{\exp(\alpha(\rho)/1 + (b/ e^{-\Phi(\rho)}) (\exp (\alpha(\rho) - 1)\} \alpha(\rho)\rho \, d\rho / {}_0\int^1 \alpha(\rho)\rho \, d\rho$$

..... (5)

The dimensionless radial velocity profile in a pore $\alpha(\rho)$ is given by,

$$d^2\alpha(\rho)/d\rho^2 + (1/\rho)\, d\alpha(\rho)/d\rho + (\beta_2/\beta_1) + 1/\beta_1\,(1 - e^{-\phi(\rho)})\,(C_A(\rho) - 1)$$

$$- (b(\rho) - 1)\,\alpha(\rho)\,C_A(\rho) / \beta_1 = 0 \qquad \text{..... (6)}$$

where $C_A(\rho) = \exp[\alpha(\rho)]/[1 + (b/e^{-\phi(\rho)})\,(\exp(\alpha(\rho)) - 1]$ ..... (7)

The boundary conditions for solving equation (6) are :

$d(\alpha(\rho))/d(\rho) = 0$ at $\rho = 0$ ..... (8)

$\alpha(\rho) = 0$ at $\rho = 1$ ..... (9)

the equation for the potential function accounting for the force exerted on an ionized solute molecule by the pore wall is,

$$\phi(\rho) = [A/R_a]/[(R_b/R_a - \rho)] \qquad \text{..... (10)}$$

where A indicates the resultant electrostatic repulsive force. Here R_a and R_b are the radii of the solvent channel and the pore in meter respectively.

The above model assumes that the solvent and the solute molecules are transported through cylindrical pores of radius R_b cutting across the skin layer of

thickness δ. SFPF model further assumes that there is an area into which the centre of the solvent molecule cannot enter due to its collision with the membrane pore wall. If the solvent is water, one can write,

$$R_h = R_a + D_w \qquad \text{..... (11)}$$

where D_w is the radius of the water molecule.

For a dilute feed solution , the average solution velocity $\alpha(\rho)_{aver}$ can be expressed as follows (Matsuura, 1994):

$$\alpha(\rho)_{aver} = \Delta p.\ R_a^2 / (8\eta D_{AB}) \qquad \text{..... (12)}$$

Here, Δp is the transmembrane pressure drop, η is the viscosity and D_{AB} is the diffusivity of the solute in the solvent.

Similarly, the potential function is averaged in an exponential form. This equivalent to averaging the solute concentration in the pore according to the Maxwell-Boltzmann equation as follows.

$$\exp[-\phi(\rho)]_{aver} = 2 \int_0^1 \exp[-\phi(\rho)]\rho\, d\rho \qquad \text{..... (13)}$$

Substituting the values of $\alpha(\rho)_{aver}$ and exp $[-\phi(\rho)]_{aver}$ from equation (12) and (13) into equation (5), the following equation is obtained:

$$f' = 1 - [\exp(\alpha(\rho)_{aver})] / [1 + (b/(\exp[-\phi(\rho)_{aver}]). (\exp[-\alpha(\rho)_{aver})] - 1] \quad \text{..... (14)}$$

The friction factor b which appears in equation (5) to (7) refers to the frictional drag experienced by a molecule while moving in a narrow pore. It is defined as the ratio of the frictional force working on the solute moving in the membrane pore to the frictional force of the bulk solution. The factor b has been expressed by the following equations.

$$b = 1 / (1 - 2.104 \lambda_f + 2.09 \lambda_f^3 - 0.95 \lambda_f^5) \quad \text{..... (15)}$$

where $\lambda_f <= 0.22$, and

$$b = 44.57 - 416.2 \lambda_f + 934.9 \lambda_f^2 + 302.4 \lambda_f^3 \quad \text{..... (16)}$$

where $\lambda_f = D / R_b$ ..... (17)

The probability density function for a normal pore size distribution with an average pore diameter R_{bmean} and a standard deviation σ is given by

$$Y(R_b) = (1/\sigma)\,(2\pi)^{0.5} \,.\, \exp\,[-(R_b - R_{bmean})^2 / 2\,\sigma^2] \qquad \ldots\ldots\ldots\ldots (18)$$

Matsuura (1994) assumed a dispersion range of $R_{bmean} \pm 3\sigma$ to account for the effect of pore on separation efficiency of isopropyl alcohol. The dispersion band which spreads over the 3σ limits of the mean value guarantees 99.7 % occurance of the random variate in this region. He divided the dispersion range into ten equal class intervals and used the mean separation efficiency for the each pore size interval. This approach is inaccurate for calculation of the average efficiency. In Monte Carlo simulation proposed here, the same $R_{bmean} \pm 3\sigma$ limits were used. However, samples outside these limits were generated and taken into account for a more complete coverage of the actual pore size distribution. In this case, the distribution function is characterised by

$$R_{blo} = R_{mean} - 3\sigma \qquad \ldots\ldots\ldots\ldots (19)$$

$$R_{bhi} = R_{mean} + 3\sigma \qquad \ldots\ldots\ldots\ldots (20)$$

$$R_{mean} = (R_{blo} + R_{bhi}) / 2.0 \qquad \ldots\ldots\ldots\ldots (21)$$

$$\sigma = (R_{bhi} - R_{blo}) / 6.0 \qquad \ldots\ldots\ldots\ldots (22)$$

Here, R_{blo} and R_{bhi} refer to the lower and the higher 3σ limits about the mean respectively. If we assume a random variate k with a uniform distribution between 0 and 1, such that :

$$Y(R_b) = 0 \quad \text{when } k = 0 \qquad \ldots\ldots\ldots (23)$$

and

$$Y(R_b) = 1/\sigma (2\pi)^{0.5} \quad \text{when } k = 1 \qquad \ldots\ldots\ldots (24)$$

Random samples of pore size were generated from R_{blo} and R_{bhi} by means of the random variate k. For this work, a random samples of 10,000 pores was generated and the separation factor was averaged over the area of the pores as follows :

$$f'_{arcav} = \sum di^2 fi / \sum di^2 \qquad \ldots\ldots\ldots (25)$$

The mean separation factors based on area was determined from equations (25) and compared with the data from the experiment for sodium chloride - water system.

6.3 Results and Discussions

The effect of pore size distribution on separation efficiency has been demonstrated theoretically by taking a random sample of 10,000 pores of mean size 6.5×10^{-10} m for cellulose acetate/ sodium chloride/ water system.

Matsuura (1994), has reported separation factor for isopropyl alcohol from an aqueous solution by cellulose acetate membrane. He assumed the mass transfer resistance to be zero such that f = f '. In this work, the same assumption has been employed for sodium chloride-water system and the physico-chemical parameters used for the calculation of the separation factor f ' are given in Table 6.1.

Table 6.1 : The physico- chemical parameters used in this work.

Viscosity of water	0.8941×10^{-3} Pa s
Diffusivity of sodium chloride	1.611×10^{-9} m^2/s
Effective radius of water molecule	0.87×10^{-10} m

Tables 6.2, 6.3 and 6.4 show the effect of pore size distribution on the separation efficiency for different feed concentrations namely 30 mg/L, 50 mg/L and 80

mg/L with different transmembrane pressure drops. The pore size distributions have the same mean of 6.5×10^{-10} m but different standard deviations. It is observed that the pore size distribution has a strong bearing upon the solute separation factor. The leakage of solute increases with a higher proportion of large pores in the skin. This is evident from the values of f and f_{areav}.

Table 6.2 : f values for experimental (feed concentration 30 mg/L) and calculated data.

Pressure Drop,ΔP (Pa)	f	
	Experimental	Calculated
227000	0.7800	0.7629
262000	0.7994	0.7857
331000	0.8216	0.8197
365000	0.8358	0.8327
400000	0.8511	0.8442
469000	0.8690	0.8629
503000	0.8749	0.8705
538000	0.8783	0.8775
606000	0.8947	0.8891
676000	0.9153	0.8989

Table 6.3 : f values for experimental (feed concentration 50 mg/L) and calculated data.

Pressure Drop,ΔP (Pa)	f	
	Experimental	Calculated
193000	0.7804	0.7354
262000	0.7908	0.7857
296000	0.8083	0.8039
331000	0.8197	0.8197
386000	0.8375	0.8399
427000	0.8513	0.8522
469000	0.8695	0.8629
503000	0.8750	0.8705
538000	0.8799	0.8775
634000	0.9079	0.8932

Table 6.4 : f values for experimental (feed concentration 80 mg/L) and calculated data.

Pressure Drop,ΔP (Pa)	f	
	Experimental	Calculated
227000	0.7711	0.7629
262000	0.7939	0.7857
331000	0.8259	0.8197
386000	0.8392	0.8399
400000	0.8577	0.8442
469000	0.8768	0.8629
503000	0.8801	0.8705
606000	0.8897	0.8891
641000	0.9061	0.8942
676000	0.9394	0.8989

It is observed that high transmembrane pressure exerts a favourable influence on the separation factor. For example (for feed concentration 30 mg/L), when the pressure drop increases from 227 kPa to 676 kPa, f_{areav} increases from 0.7629 to 0.8989 as shown in Table 6.2. Matsuura (1994) has proposed a numerical integration scheme to take normal pore size distribution into account between the $\pm 3\sigma$ limits. This is an approximation due to the fact that it does not take into account the effect of large and small pores which exist outside the two limits.

The fine pores which are smaller than ($R_{bmean} - 3\sigma$) do not exert significant influence on the separation efficiency, while the pores which are larger than ($R_{bmean} + 3\sigma$) have a strong influence. Thus the larger pores have a deleterious effect on solute separation and strongly affect the separation factor.

6.4 Conclusion

It is observed that pore size distribution has a strong bearing upon the solute separation factor. Large pores increase the leakage of solute molecules through the membrane and reduce it's efficiency. However, higher transmembrane pressure affects the separation factor favourably. This is an expected phenomenon and implies that a high transmembrane pressure enhances the flow of water molecules more favourably than that of the solute sodium chloride.

The major shortcoming of the analysis proposed by Matsuura (1994) is that it does not take into account the contribution of individual pores and in particular the large ones which lie outside the 3σ limit. This approximation leads to error and could be overcome by the Monte Carlo technique.

In this work, it has been shown that Monte Carlo simulation has some advantages over the numerical integration scheme for the Gaussian pore size distribution as suggested by Matsuura (1994). These include the determination of the effect of separation efficiency on pores outside the 3σ limits. It is also possible to take into account non-circular pore geometry into account.