

Finely Porous Models and Radially Averaged Friction Factors

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SYNOPSIS

The finely porous (FPM) and modified finely porous (MD-FPM) models were used to generate sieving curves for the permeation of polyethylene glycol solutions through a nanofiltration membrane. The curves were calculated at five different operating pressures. Both models use Faxen's equation to calculate the friction factor b^{-1} . Faxen's equation represents the friction between a solute molecule translating along the centerline of a cylindrical pore and the pore wall. The resulting sieving curves were quite different from the typical sigmoidal curves found in ultrafiltration. The departure from this typical shape, was considerable at the lower pressures used in nanofiltration and was less pronounced at the higher pressures found in reverse osmosis. Reasonable sieving curves were obtained when Faxen's equation was radially averaged. Differences in PEG separation of 22 to 32% were obtained between the averaged and the centerline approaches. The partition coefficient K was predicted, for sucrose, raffinose, and NaCl. The use of centerline values of the friction factor led to the overestimation of solute rejection by a factor of 1.24 to 3.11. Finally, in both the FPM and MD-FPM models, centerline correlations of the friction factor, b^{-1} , must be multiplied by $(1 - \lambda)^2$ in order to be consistent with other averaged quantities.

INTRODUCTION

The variety and performance of synthetic membranes has increased considerably during the past decade. A substantial part of this change has occurred through the commercialization of nanofiltration (NF) membranes. These membranes have pore sizes in the intermediate range between those found in hyperfiltration (HF) and ultrafiltration (UF). The use of NF membranes is increasing due to their superior permeation rates over HF membranes.

Nanofiltration membranes have been successfully used in wastewater recovery, oil-water separations, the removal of low molecular weight organics, surface water treatment for color and humic acid removal, water softening, the concentration of fruit juices, the dealcoholization of beer and wine, and the reclamation of metals from rinse waters. Many

of these applications involve the separation of solutes that are too small to be effectively retained by ultrafiltration membranes and that do not require the high solute rejection characteristics of hyperfiltration membranes. In many of these applications, the separation of solute is not limited by the osmotic pressure of the feed solution.

In general, nanofiltration membranes are used at much lower pressures than hyperfiltration or reverse osmosis membranes. Typical operating pressures range from 300 to 3000 kPa in nanofiltration, while they are 3000 to 10,200 kPa in hyperfiltration. The transport of solute through a membrane is greatly influenced by pressure. The validity of porous models to describe the transport of solutes through nanofiltration membranes must be tested at the lower operating pressures used in the nanofiltration processes.

Since nanofiltration membranes have pores of intermediate size, their sieving curves should display the characteristic sigmoidal shape found in ultrafiltration membranes. Sieving curves for polyethylene glycols (PEG) were predicted from the finely porous model (FPM) proposed by Merten,¹ and the modified finely porous model (MD-FPM) recently proposed by Mehdizadeh and Dickson.² In both models,

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radially dependent variables, such as the solute and solvent velocities, concentrations, and partition coefficients are radially averaged or obtained as the result of a radially averaging procedure. The only variable that is not averaged is the solute-membrane friction factor. Both models use the centerline value of the friction factor, derived by Faxen.³ The effect of radially averaging this factor on solute separation and the partition coefficient, K , will be discussed.

THEORY

The Finely Porous Model (FPM)

The derivation of this transport model is attributed to Merten.¹ In this approach, tortuous paths through the selective layer of a membrane are modeled as an array of capillaries running perpendicular to the surface of the membrane. The model takes into account a reduction in the average flowrate due to the friction of solute with the pore wall. In Merten's derivation, the total pore length is the product of pore tortuosity and membrane thickness. In this work, the total pore length is represented by the value δ . Derivations were performed on a single pore, which implies that the fractional open area of the porous membrane ϵ in Ref. 1, is unity ($\epsilon = 1.0$).

A force and momentum balance on a solute, translating through a membrane pore (see Fig. 1), yields the following equation for solute flux:

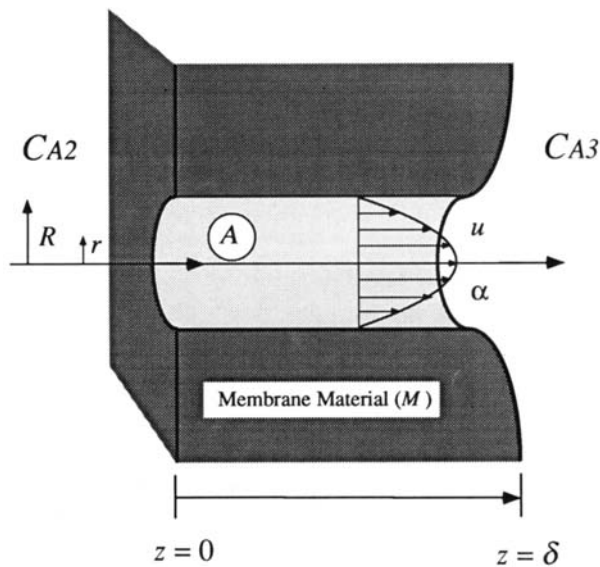


Figure 1 Pore through the selective layer of a membrane.

$$J_A = -\frac{1}{b} \frac{RT}{\chi_{AB}} \frac{dc_A(z)}{dz} + \frac{1}{b} c_A(z) \epsilon \quad (1)$$

The solute to membrane interaction parameter b is defined as;

$$b \equiv \frac{\chi_{AB} + \chi_{AM}}{\chi_{AB}} \quad (2)$$

where

$$\chi_{AB} = \frac{RT}{D_{AB}} \quad (3)$$

The equilibrium distribution coefficients K_2 and K_3 are defined from the following boundary conditions:

At the pore entrance $z = 0$,

$$c_{A|z=0} = K_2 C_{A2} \quad (4)$$

and at the pore exit $z = \delta$,

$$c_{A|z=\delta} = K_3 C_{A3} \quad (5)$$

The equation for solute flux, eq. (1), is solved with the boundary conditions given by eqs. (4) and (5), and the Taylor-Aris assumption that the average axial solute and solvent velocities are equal.⁴⁻⁶ The solution can be rearranged to give the following expression for the ratio of the concentration at the exit of the membrane pore C_{A3} to that at the pore entrance C_{A2} :

$$\frac{C_{A3}}{C_{A2}} = \frac{K_2/b \exp(v\delta\chi_{AB}/RT)}{K_3/b + [\exp(v\delta\chi_{AB}/RT) - 1]} \quad (6)$$

The velocity profile within membrane pores is assumed to be parabolic. Corrections to Poiseuille's law are included in order to account for the reduction in permeability due to frictional forces between the solute and membrane material.

The average solute velocity v is expressed as:

$$v = H \left[\frac{1}{(1 + (H\chi_{AM}/M_A)C_{A3})} \right] \frac{\Delta P}{\delta} \quad (7)$$

The value of the hydrodynamic permeability, H , is given by,

$$H = \frac{R^2}{8\eta} \quad (8)$$

The transmembrane pressure, ΔP , includes the difference in osmotic pressure across the membrane. For atmospheric permeate discharge:

$$\Delta P = P_g - \pi(C_{A3}) + \pi(C_{A2}) \quad (9)$$

In this model, the value of the friction factor b^{-1} is obtained directly from Faxen's equation:

$$b^{-1} = 1 - 2.1044\lambda + 2.089\lambda^3 - 0.948\lambda^5 \quad (10)$$

The true solute separation f' , based on the boundary layer concentration C_{A2} is expressed as follows:

$$f' = 1 - \frac{C_{A3}}{C_{A2}} \quad (11)$$

For a given a solute-solvent-membrane system, membrane pore radius, operating pressure, and feed concentration, eqs. (6) to (11) can be solved to obtain a mathematically unique value for solute separation.

The Modified Finely Porous Model (MD-FPM)

The finely porous model has recently been modified by Mehdizadeh and Dickson.² This model is derived from the same basic principles as the FPM, but it uses a different solute material balance. The expression for the ratio of the concentration at the exit of the membrane pore C_{A3} to that at the pore entrance C_{A2} is given by:

$$\frac{C_{A3}}{C_{A2}} = \frac{K_2/b \exp(\alpha)}{K_3/b + [\exp(\alpha) - 1]} \quad (12)$$

Solute separation is then obtained from eq. (11) as follows:

$$f' = \frac{(1 - K_2/b)\exp(\alpha) - (1 - K_3/b)}{[\exp(\alpha) - 1] + K_3/b} \quad (13)$$

The value of α is given by:

$$\alpha = H\left(\frac{\chi_{AB}}{RT}\right) \left\{ \Delta P - \pi_2(1 - K_2) + \pi_3(1 - K_3) - \alpha\left(\frac{K_2}{b}\right)(b - 1) \times \left[\pi_2 + \frac{\pi_2 - (K_3/K_2)\pi_3}{\exp(\alpha) - 1} \right] \right\} \quad (14)$$

As in the FPM model, values for the friction factor, b^{-1} , are taken directly from Faxen's equation (eq. 10).

Averaging of the Friction Factor b^{-1}

The friction factor, derived on theoretical grounds by Faxen,³ represents the friction or drag on a solute molecule moving along the central axis of a cylindrical pore. This factor must be radially averaged over the entire pore area in order to be consistent with other radially averaged quantities, such as v , α , C_{A3} , K_2 , and K_3 . It is normally assumed that centerline friction factors are applicable to all radial positions in the pore. This is known as the "centerline approximation." The averaging of centerline interaction terms has been performed in other, similar transport models.^{7,8}

Radially averaging centerline value of the friction factor, b^{-1} , over the pore area available for solute transport, yields:

$$\bar{b}^{-1} = \frac{\int_0^{1-\lambda} b^{-1} \rho d\rho}{\int_0^1 \rho d\rho} = (1 - \lambda)^2 b^{-1} \quad (15)$$

The values of b^{-1} and \bar{b}^{-1} were used to calculate solute separation for the FPM and MD-FPM models.

EXPERIMENTAL

A predictive equation for the radius of PEG in water, as a function of molecular weight, was obtained by combining data from Refs. 9 and 10. Solute radius, a_s , obtained from Ref. 9, and the unperturbed radius of gyration from Ref. 10 vs. the square root of the molecular weight of PEG at 25°C, were found to be linearly correlated. Equation (16) is valid in the range of 200 to 37,640 Kg/kmol.

The solute radius of PEG was calculated as follows:

$$a_s(\text{nm}) = 0.026068 [\text{PEG mol wt (Kg/kmol)}]^{1/2} - 0.015 \quad \text{for } r^2 = 1.000 \quad (16)$$

The diffusivity of PEG was correlated with the inverse of the solute radius, using the data from Ref. 11, taken at 25°C, the following equation was obtained:

$$D_{AB}(\text{m}^2/\text{s}) = \frac{0.24424 \times 10^{-9}}{a_s(\text{nm})} \quad \text{for } r^2 = 1.000 \quad (17)$$

The osmotic pressure of dilute aqueous solutions containing nonelectrolytes can be evaluated from van't Hoff's equation:

$$\pi(C_A) = RT \times C_A \quad (18)$$

The separation of PEG vs. molecular weight was calculated for a membrane having a 1.5 nm pore radius at operating pressures of 100, 300, 1000, 3000, and 6000 kPa. The concentration of the boundary layer C_{A2} was taken as 0.2 Kg/m³. Equations (16), (17), and (18), and steric interaction ($K_2 = K_3 = 1$) were used in all calculations involving PEGs.

The data used in the calculation of solute separation and K , for sucrose, raffinose, and sodium chloride are as follows: for sucrose $a_s = 0.51$ nm,¹² $D_{AB} = 0.56 \times 10^{-9}$ m²/s,⁹ for raffinose $a_s = 0.65$ nm,¹² $D_{AB} = 0.41 \times 10^{-9}$ m²/s,⁹ and NaCl $a_s = 0.152$ nm,¹³ $D_{AB} = 1.61 \times 10^{-9}$ m²/s.¹³

Computations

The following section lists the computational steps involved in evaluating solute separation.

For the FPM model, solute separation was calculated as follows:

1. Assume C_{A3} ,
2. Calculate v from eqs. (7), (8), and (9),
3. Substitute v into eq. (6),

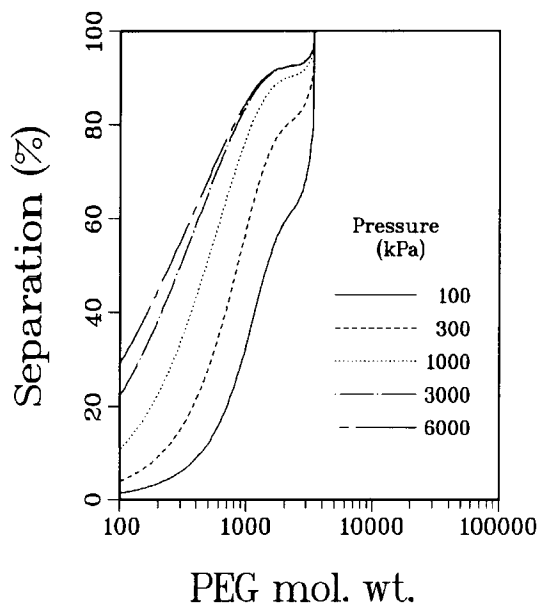


Figure 2 Separation of PEG vs. molecular weight for the FPM model, using Faxen's equation as the friction factor.

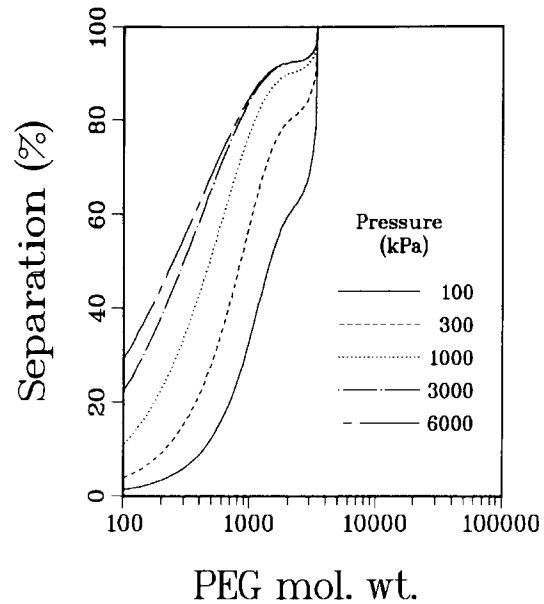


Figure 3 Separation of PEG vs. molecular weight for the MD-FPM model, using Faxen's equation as the friction factor.

4. Check that both sides of eq. (6) are within a specified tolerance,
5. If both sides are not, assume a new C_{A3} and repeat steps 2 to 4,
6. If both sides are within a specified tolerance, calculate solute separation from eq. (11).

For the MD-FPM model, solute separation was calculated as follows:

1. Assume C_{A3} ,
2. Calculate α iteratively from eq. (14),
3. Substitute α into eq. (12),
4. Check that both sides of eq. (12) are within a specified tolerance,
5. If both sides are not, assume a new C_{A3} and repeat steps 2 to 4,
6. If both sides are within a specified tolerance, calculate solute separation from eq. (11).

Tolerances for the computational convergence of C_{A3}/C_{A2} and α were set at 1.0×10^{-10} .

RESULTS AND DISCUSSION

Sieving curves for PEG, based on centerline values of the friction factor, are shown in Figure 2 for the FPM and Figure 3 for the MD-FPM models. The curves were generated by substituting Faxen's

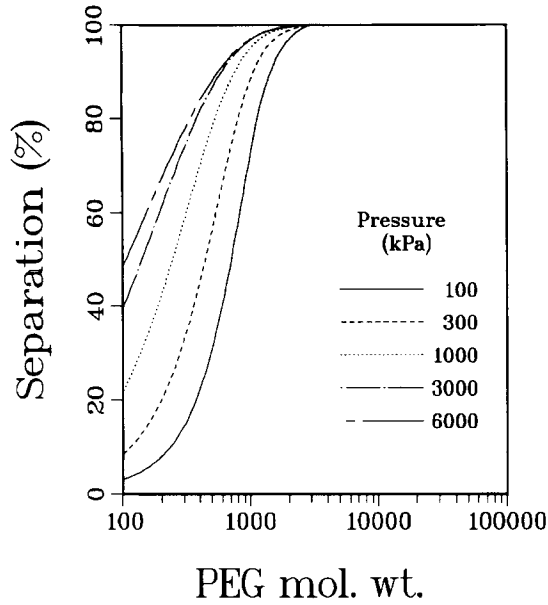


Figure 4 Separation of PEG vs. molecular weight for the FPM model, using the radially averaged friction factor.

equation for the friction factor b^{-1} . The curves have two points of inflection and do not display the characteristic sigmoidal shape found in ultrafiltration sieving curves. The results indicate that, for both models, deviations are accentuated at lower pressures. However, the shape of the curve is only slightly better at the higher pressures found in hyperfiltration.

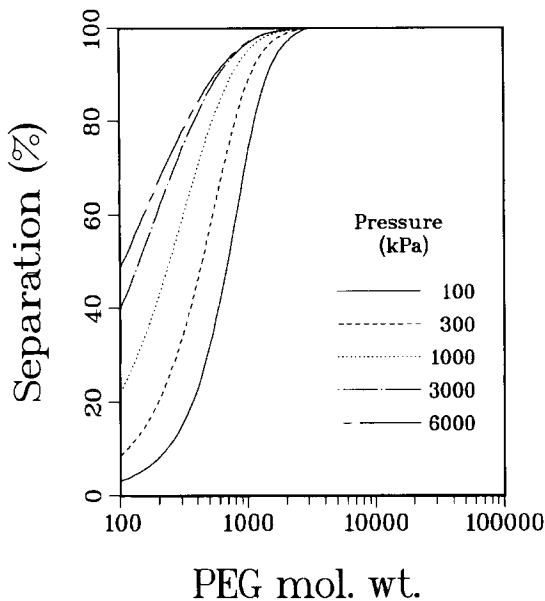


Figure 5 Separation of PEG vs. molecular weight for the MD-FPM model, using the radially averaged friction factor.

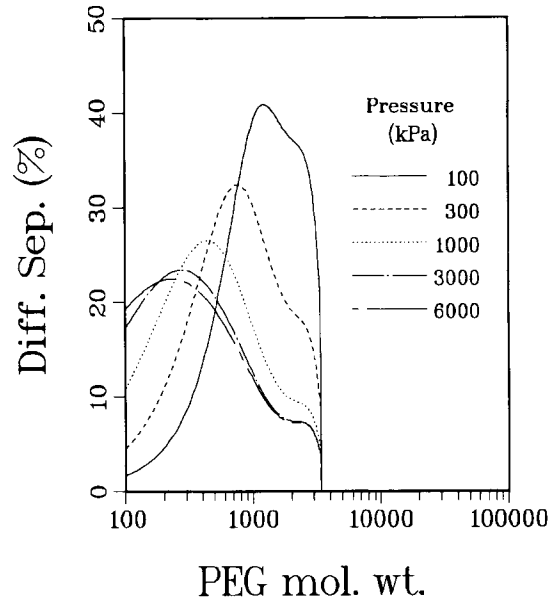


Figure 6 Difference in separation as defined by eq. (19) vs. PEG molecular weight for the FPM model.

The irregular shape of the curve is obviously due to limitations in Faxen's equation. This equation is only valid for $0 < \lambda < 0.4$, and it provides very rough estimates for $0.4 < \lambda < 1.0$. This is not a very serious problem in reverse osmosis where, for sodium chloride, λ is less than 0.4. Other centerline correlations of the friction factor have been used with the FPM model and do provide smoother sieving curves.¹⁴ However, as the object of this work is to demonstrate

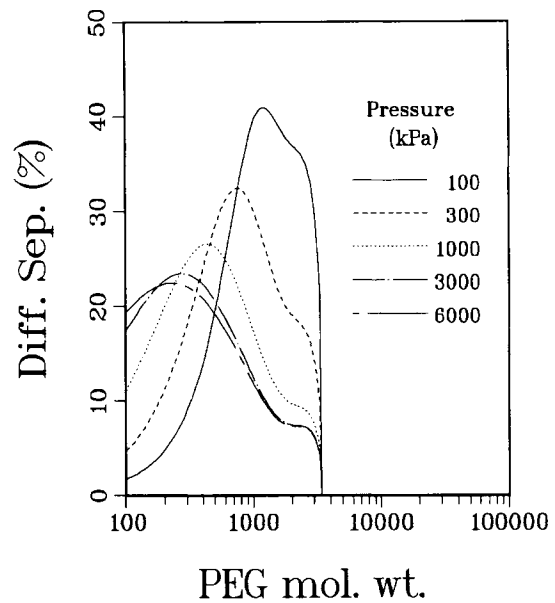


Figure 7 Difference in separation as defined by eq. (19) vs. PEG molecular weight for the MD-FPM model.

Table I Separation and Predicted Values of K for the NF40 Membrane Using the FPM Model

Solute	λ	Separation (%) for $K = 1$		Prediction of K^a			
		b^{-1}	\bar{b}^{-1}	Sep. % ^b	K		Ratio = $K(\bar{b}^{-1})/K(b^{-1})$
					b^{-1}	\bar{b}^{-1}	
Sucrose	0.34	47.52	72.79	98	0.02980	0.06818	2.29
Raffinose	0.43	66.18	88.00	99	0.02678	0.08318	3.11
NaCl	0.10	5.75	11.16	45	0.27505	0.33506	1.22

^a Values of K calculated for the permeation of a 2.0 Kg/m³ solution, at 1550 kPa, through a membrane having a pore radius of 1.5 nm, based on separation data for the NF40 membrane.¹⁵

^b Separation data for the NF40 membrane.¹⁵

the effects of radial averaging, the discussion was limited to the use of Faxen's equation as a friction factor.

Curves generated with the radially averaged value of \bar{b}^{-1} are shown in Figure 4 for the FPM and Figure 5 for the MD-FPM models. The curves have a single point of inflection and display the typical sigmoidal shape found in ultrafiltration sieving curves.

The difference in separation obtained from both approaches is shown in Figures 6 and 7 for the FPM and MD-FPM models, respectively. The ordinates of both plots are calculated for a given molecular weight as follows:

$$\text{Diff. Sep. (\%)} = \text{Sep.}(\bar{b}^{-1}) - \text{Sep.}(b^{-1}) \quad (19)$$

These plots indicate that centerline values of b^{-1} underestimate solute separation. Even at the higher pressures used in hyperfiltration, differences in solute separation of up to 22% are obtained. The differences increase as the applied pressure decreases and reaches 32% for the 300 kPa pressure.

The value of K was predicted for sucrose, raffinose, and NaCl, based on manufacturers specifications for the NF40 membrane produced by Dow Chemical Co.¹⁵ This membrane is said to have performance characteristics between those of RO and UF membranes. For demonstration purposes, a pore radius of 1.5 nm is a reasonable estimate for this type of membrane. This pore size estimate is for demonstration purposes only and there is no attempt here to ascertain this value. At 1550 kPa (225 psi), the NF40 is reported to separate sucrose at 98%, raffinose at 99% and NaCl at 45%.¹⁵

The separation of sucrose, raffinose, and NaCl was determined for the 1.5 nm pore size, at 1550 kPa operating pressure, and $K_2 = K_3 = K = 1$ for the FPM model, Table I, and the MD-FPM model, Table II. As with PEGs, the separation based on centerline values of the friction factor were always lower than those obtained from radially averaged values. Differences in solute separation ranged from 5 to 25%.

Both transport models were used to predict K

Table II Separation and Predicted Values of K for the NF40 Membrane Using the MD-FPM Model

Solute	λ	Separation (%) for $K = 1$		Prediction of K^a			
		b^{-1}	\bar{b}^{-1}	Sep. % ^b	K		Ratio = $K(\bar{b}^{-1})/K(b^{-1})$
					b^{-1}	\bar{b}^{-1}	
Sucrose	0.34	48.61	74.11	98	0.02985	0.06853	2.30
Raffinose	0.43	66.92	88.47	99	0.02681	0.08349	3.11
NaCl	0.10	5.93	11.80	45	0.27912	0.34562	1.24

^a Values of K calculated for the permeation of a 2.0 Kg/m³ solution, at 1550 kPa, through a membrane having a pore radius of 1.5 nm, based on separation data for the NF40 membrane.¹⁵

^b Separation data for the NF40 membrane.¹⁵

based on the separation data for the NF40 membrane. These results can be found in Table I for the FPM, and Table II for the MD-FPM model. Values of $K < 1.0$ indicate that solute is rejected from the membrane material. All the predicted values of K were less than 1.0, which is expected for sucrose, raffinose, and NaCl.

For a given solute, the lower the magnitude of K the greater the solute that is rejected from the membrane material. For both models, the values of K obtained from radial averaging (\bar{b}^{-1}) were always superior to those obtained from centerline values (b^{-1}). This is a direct result of the lower separation predicted by centerline values of the friction factor. In order to obtain the same separation, solute must be rejected to a greater extent in the centerline approach than in the averaged one. The value of K obtained from centerline values of the friction factor was overestimated by a factor of 1.24 to 3.11, see Tables I and II. Following the same reasoning, should the solute be attracted by the membrane, the solute-membrane material interaction will be underestimated in the centerline approach.

CONCLUSIONS

The friction factor b^{-1} must be multiplied by $(1 - \lambda)^2$ in order to be consistent with other radially averaged quantities present in the FPM and MD-FPM models. Failure to do this will cause the models to underestimate solute separation by 22 to 32%, for a membrane having a 1.5 nm pore radius. If the magnitude of the solute to membrane material interaction is to be determined from the separation data, the use of these models in their present form will lead to the overestimation of this interaction. Conversely, it will lead to the underestimation of the interaction if solute is attracted to the membrane material.

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NOMENCLATURE

Descriptors

A ,	Solute,
B ,	Solvent,
M ,	Membrane material,
1,	Bulk feed solution,
2,	Boundary layer,
3,	Bulk permeate solution.

Alphabetical

a_s ,	Stokes Einstein radius (nm),
b ,	Solute to membrane interaction parameter (dim),
b^{-1} ,	Friction factor based on centerline factor, $\bar{b}^{-1} = (1 - \lambda)^2 b^{-1}$ (dim),
C_{ai} ,	Concentration of solute (kmol/m ³),
$c_A(z)$,	Concentration of solute at position (z) in the pore (kmol/m ³),
D_{AB} ,	Bulk solution diffusion coefficient (m ² /sec),
f' ,	True solute separation based on the boundary layer conc. (dim),
H ,	Hydrodynamic permeability (m ³ /sec/Kg),
J_A ,	Molar flux of solute, (kmol/m ² /sec),
$K_i = K$,	pore partition coefficient defined by eqs. (4) and (5),
M_A ,	Molecular weight of solute A (Kg/kmol),
P_g ,	Operating or gauge pressure for atmospheric permeate discharge (kPa),

ΔP ,	Effective transmembrane pressure (kPa),	η ,	Solution viscosity ($\text{Kg m}^{-1}\text{sec}^{-1}$),
R ,	Effective or hydrodynamic membrane pore radius (m),	δ ,	Total pore length = pore tortuosity \times membrane thickness (m),
\underline{R} ,	Gas constant (kJ/kmol K),	ψ_{AM} ,	Proportionality constant defined by eq. (2) ($\text{kJ sec/m}^2\text{ kmol}$),
r ,	Radial distance (m)	ψ_{AB} ,	Proportionality constant defined by eq. (3) ($\text{kJ sec/m}^2\text{ kmol}$),
T ,	Temperature ($^{\circ}\text{K}$)	ϵ ,	Fractional open area of the porous membrane (dim),
u ,	Solute velocity with respect to the pore wall (m/sec),	λ ,	Ratio of the solute radius to the pore radius = g_s/R (dim),
z ,	Axial distance from the pore inlet, in cylindrical coordinates (m).	$\pi(C_{Ai})$,	Osmotic pressure of solution at concentration $C_{Ai}, i = 1, 2, 3$ (kPa),
Greek Letters		π_i ,	Osmotic pressure of solution at $i = 1, 2, 3$ (kPa),
α ,	Dimensionless solution velocity defined by eq. (14) (dim),	ρ ,	Radial distance = r/R (dim).