Theoretical Modification of the Finely Porous Model for Reverse Osmosis Transport

H. MEHDIZADEH and J. M. DICKSON*

Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7

SYNOPSIS

One of the most significant models used to describe and predict the performance of reverse osmosis type membranes is the finely porous model (FPM). In this paper, the basic assumptions of the model are examined and modified. The two most serious problems with FPM are that an incorrect form of material balance on the solute is used and that the osmotic pressure effects are not completely taken into account for electrolytes. A modified model (called MD-FPM), which is based on the same physical precepts is derived. Equations describing the concentration profile for both models have been derived and compared. It has been shown that the FPM can predict physically unacceptable results. Difficulties in using the parameters from the model for prediction or for membrane development work are discussed. Simulation results for the MD-FPM model are consistent with what is expected for reverse osmosis type membranes.

INTRODUCTION

The finely porous model (FPM) was proposed originally by Merten.[1] In this model transport of solute and solvent occurs in small 1-dimensional pores. A balance of applied and frictional forces is used to describe the flow of solute inside the pores, as proposed by Spiegler.[2] In principle, the solute partition coefficient K can be different on the high-pressure side and low-pressure side of the membrane. This form is known as FPM-4, implying that the model has four parameters. Often the partition coefficient is assumed to be the same on each side of the membrane ($K_2 = K_3 = K$) to give a three-parameter model (FPM-3). A complete derivation of the model (FPM) has been given by Jonsson and Boesen[3] and by Soltanieh and Gill.[4]

In this paper, we examine the theoretical aspects of the FPM-3 and FPM-4 relationships. Some important limitations in these models are removed and the new modified models, called the *modified* FPM-3 (MD-FPM-3) and the *modified* FPM-4 (MD-FPM-4) relationships, are derived. The mathematical formulation of the model is done for the general case of the MD-FPM-4 relationship, and then the MD-FPM-3 relationship is derived from the general relationship.

In this paper, only simulation results for the models are shown, and real predictions will be discussed in a future paper.

THEORY

The modified finely porous models (i.e., the three- and four-parameter forms) are derived here in a manner similar to the derivation of the original models. First, the equation of solute flux together with the equation of solute material balance are examined. Then, the equation of fluid velocity through the pores are derived, and finally, the equations required to describe the overall flux and separation are presented.

Since these FPM models assume that the pores are 1-dimensional, then conditions vary only with axial position through the pore. Compared to a 2-dimensional model, these conditions at any axial position represent the radially averaged values. For instance, $C_A(z)$ represents the radially average concentration of A in the pore at position z (see Fig. 1).
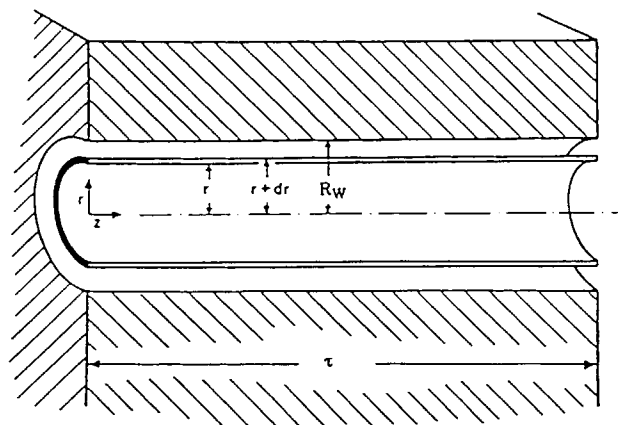
Figure 1 The cylindrical coordinate system in a membrane pore.

The Equations of Solute Flux and Solute Material Balance

Since the pore is relatively long (i.e., with respect to its radius), the solution velocity profile is assumed to be fully developed. Then, similar to the FPM, the equation of solute flux is obtained, from a force balance on the solute in the pore,[3] as

$$J_A = -\frac{RT}{\chi_{AB}b}\frac{dC_A(z)}{dz} + \frac{C_A(z)u}{b} \qquad (1)$$

where

$$\chi_{AB} = -\frac{F_{AB}}{u_A - u_B} = \frac{RT}{D_{AB}} \qquad (2)$$

$$b = \frac{\chi_{AB} + \chi_{AM}}{\chi_{AB}} = \frac{D_{AB}}{D_{AM}} \qquad (3)$$

Equation (1) is true for the case of nonelectrolytes. However, for the case of strong electrolytes, the equation of salt flux is derived, in Appendix A [eq. (A.7)], as

$$J_A = \frac{1}{b}\left[-\frac{1}{\chi_{AB}}\frac{d\pi(z)}{dz} + \frac{\pi(z)u_B}{RT} \right] \qquad (4)$$

where $\pi(z)$ is the osmotic pressure of the solution at z inside the pore.

The correct way of using the above differential flux equation is to write the differential material balance in the pore, substitute in the flux equation, and solve the resulting second-order differential equation subject to boundary conditions at the pore inlet and outlet. The general boundary conditions

are given by the definition of the solute partition coefficient:

i. At the pore inlet,

$$C_A(z = 0) = C_{A2}K_2 \qquad (5)$$

ii. At the pore outlet,

$$C_A(z = \tau) = C_{A3}K_3 \qquad (6)$$

The differential material balance states that the divergence of solute flux vector at steady state is zero,

$$\nabla \cdot \mathbf{J}_A = 0 \qquad (7)$$

where ∇ is the del vector differential operator. In 1-dimensional form, eq. (7) becomes

$$\frac{dJ_A}{dz} = 0 \qquad (8)$$

Then, combining eqs. (1) [or eq. (4) for electrolytes] and (8) gives the following second-order differential equations:

$$\frac{d^2C_A(\xi)}{d\xi^2} - \alpha\frac{dC_A(\xi)}{d\xi} = 0 \qquad (9)$$

$$\frac{d^2\pi(\xi)}{d\xi^2} - \alpha\frac{d\pi(\xi)}{d\xi} = 0 \qquad (10)$$

where

$$\alpha = \frac{u\tau\chi_{AB}}{RT} = J_V\left(\frac{\tau}{\epsilon}\right)\frac{\chi_{AB}}{RT} \qquad (11)$$

and

$$\xi = z/\tau \qquad (12)$$

subject to the boundary conditions, eqs. (5) and (6). Equation (10) is equivalent to eq. (9) for dilute solutions of electrolytes. The parameter α, which is the dimensionless fluid velocity in the membrane pore, represents the ratio of convection to molecular diffusion forces. Equation (9) has been solved analytically in Appendix B [eq. (B.4)] to give the concentration profile in the pore, in the MD-FPM-4 relationship, as

$$C_A(\xi)$$

$$= \left\{ C_{A2} - \left(C_{A2} - \frac{K_3}{K_2} C_{A3} \right) \left[\frac{1 - \exp(\alpha\xi)}{1 - \exp(\alpha)} \right] \right\} K_2 \quad (13)$$

Now, substituting the concentration profile into the solute flux eq. (1), or eq. (4), gives an explicit expression for the solute flux in terms of the dimensionless velocity and the partition coefficients:

$$J_A = \frac{\alpha}{\tau \chi_{AB} b} \left[\pi_2 + \frac{\pi_2 - (K_3/K_2)\pi_3}{\exp(\alpha) - 1} \right] K_2 \quad (14)$$

as derived in Appendix A.

The above approach can be compared to that used in the finely porous model. In the FPM relationship, the following material balance in the pore has been proposed:

$$J_A = C_{A3} u \quad (15)$$

This equation was combined with eq. (1) to give a first-order differential equation, which was solved using the boundary condition at the pore inlet [eq. (5)]. The resulting equation was substituted into the second boundary condition [eq. (6)] and rearranged to give an expression for separation, f'.

The separation f' compares the concentration at the boundary layer above the membrane, C_{A2}, with the permeate concentration, C_{A3}, and is the theoretical separation obtained in the absence of concentration polarization. Therefore, the separation f' is defined, for dilute solutions, as

$$f' = \frac{C_{A2} - C_{A3}}{C_{A2}} \quad (16)$$

The relationship between f' and α, for the FPM-4 relationship, has been derived in Appendix B as

$$f' = \frac{(1 - K_2/b) \exp(\alpha) - (1 - K_3/b)}{[\exp(\alpha) - 1] + K_3/b} \quad (17)$$

The problems with the above method (i.e., the finely porous model) are as follows:

i. Equation (15) ignores the diffusive contribution to solute flux and considers only the convective contribution; this violates the physical facts in eq. (1).

ii. Equation (15) ignores the distinction between concentrations inside and outside the pore; a velocity inside the pore is combined with a concentration outside the pore.

The result of these errors is that the finely porous model calculates the concentration and concentration gradient in the pore incorrectly (note that the same mistake exists in the surface force-pore flow (SF-PF) model of reverse osmosis[5]). The equation of concentration profile in the pore (in FPM) has not been shown in the literature; however, its derivation is straightforward and is shown in Appendix B.

Equation of Dimensionless Fluid Velocity in MD-FPM

As a first step, the Poiseuille expression of fluid velocity is modified for the pore fluid to include the frictional force between the solute and the pore wall,[3]

$$J_V = \frac{\epsilon R_W^2}{8\eta} \left[-\frac{dP(z)}{dz} - \chi_{AM} u_A C_A(z) \right] \quad (18)$$

where

$$J_V = \epsilon u \quad (19)$$

and ϵ is the fractional pore area which corrects the fluid velocity in a single pore to the volumetric permeation flux for a whole membrane.

Within a pore, the flux and the velocity of solute are related as

$$J_A = u_A C_A(z) \quad (20)$$

and J_A is given by eq. (14). On the other hand, the pressure gradient term, $-dP/dz$, can be well approximated by[5]

$$-\frac{dP(z)}{dz}$$

$$\quad (21)$$

$$= \frac{1}{\tau} [\Delta P - \pi_2(1 - K_2) + \pi_3(1 - K_3)]$$

which is similar to that in the FPM[3] and ΔP is the pressure drop across the membrane. Then, using eqs. (19)–(21) together with eq. (14), eq. (18) becomes

$$\alpha = \frac{R_W^2}{8\eta} \left(\frac{\chi_{AB}}{RT} \right) \left\{ \Delta P - \pi_2(1 - K_2) \right.$$

$$+ \pi_3(1 - K_3) - \alpha \left(\frac{K_2}{b} \right)(b - 1) \quad (22)$$

$$\times \left[\pi_2 + \frac{\pi_2 - (K_3/K_2)\pi_3}{\exp(\alpha) - 1} \right] \right\}$$

Under the special case $\alpha \ll 1$, where

$$\exp(\alpha) \approx \alpha + 1 \tag{23}$$

then α can be derived from eq. (22) as

$$\alpha = (R_W^2/8\eta)(\chi_{AB}/RT)$$
$$\times \frac{\{\Delta P - (1 - K_2/b)\pi_2 + (1 - K_3/b)\pi_3\}}{1 + (R_W^2/8\eta)(\chi_{AB}/RT)(K_2/b)(b-1)\pi_2} \tag{24}$$

If this condition [i.e., eq. (23)] is not met, then α is implicit in eq. (22) and can be determined by trial and error.

Relationships for the Solute and Solvent Fluxes through the Membrane and Separation in MD-FPM

The solute and solvent fluxes through the membrane are related to the corresponding fluxes through a single pore as

$$N_A = \epsilon J_A \tag{25}$$

$$N_B = \epsilon J_B \tag{26}$$

where J_A is given by eq. (14) and

$$J_B = u_B C = \left(\frac{CRT}{\tau \chi_{AB}}\right)\alpha_B \tag{27}$$

where the dimensionless solvent velocity α_B is defined by eq. (A.9) in Appendix A. The total permeation flux through the membrane is

$$N_T = (N_A + N_B) = \epsilon(J_A + J_B) \tag{28}$$

Using eqs. (14) and (27), the above equation becomes

$$N_T = \frac{1}{\chi_{AB}}\left(\frac{\alpha}{\tau/\epsilon}\right)\left\{\left[\pi_2 + \frac{\pi_2 - (K_3/K_2)\pi_3}{\exp(\alpha) - 1}\right]\frac{K_2}{b} + CRT\left(\frac{\alpha_B}{\alpha}\right)\right\} \tag{29}$$

However, from eq. (11),

$$J_V = \frac{\alpha}{(\tau/\epsilon)(\chi_{AB}/RT)} \tag{30}$$

Also,

$$N_T = CJ_V \tag{31}$$

Then using eqs. (30) and (31), eq. (29) is employed to determine the ratio of solvent to solution velocities as

$$\frac{\alpha_B}{\alpha} = 1 - \frac{1}{CRT}\left[\pi_2 + \frac{\pi_2 - (K_3/K_2)\pi_3}{\exp(\alpha) - 1}\right]\frac{K_2}{b} \tag{32}$$

Now, using the relationship

$$C_{A3} = C\left(\frac{N_A}{N_A + N_B}\right) = C\left(\frac{1}{1 + J_B/J_A}\right) \tag{33}$$

and using eqs. (14) and (27), eq. (33) becomes

$$\frac{J_B}{J_A} = CRT\left(\frac{\alpha_B}{\alpha}\right)$$
$$\times \left\{\left[\pi_2 + \frac{\pi_2 - (K_3/K_2)\pi_3}{\exp(\alpha) - 1}\right]\frac{K_2}{b}\right\}^{-1} \tag{34}$$

Combining eqs. (33) and (34) then gives

$$C_{A3} = C\left(1 + CRT\left(\frac{\alpha_B}{\alpha}\right)\right.$$
$$\left. \times \left\{\left[\pi_2 + \frac{\pi_2 - (K_3/K_2)\pi_3}{\exp(\alpha) - 1}\right]\frac{K_2}{b}\right\}^{-1}\right) \tag{35}$$

Finally, substituting for (α_B/α) from eq. (32) in eq. (35), the following relationships are derived for separation:

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

for nondissociating solutes

$$= \frac{[1 - (\nu^+ + \nu^-)K_2/b]\exp(\alpha)}{[\exp(\alpha) - 1] + (\nu^+ + \nu^-)K_3/b} \tag{36}$$

for strong electrolytes

The above equation, which is valid only under the restriction of eq. (23), is compared to that in FPM given by eq. (17). That is, under this restriction [of eq. (23)], Equations (17) and (36) are the same for nondissociating solutes and differ significantly for dissociated electrolytes.

To determine the numerical values of separation in the above equations, the value of α is needed

which can be determined from eq. (24); however, π_3 (and therefore f') is also needed. Therefore, these equations are coupled and can be solved by a trial and error technique.

Because $[\exp(\alpha) - 1]$ is always greater than 0 then,

$f' > 0$ (positive separation) when

$K/b < 1$ (for nondissociating solutes)

$K/b < 1/(\nu^+ + \nu^-)$ (for strong electrolytes)

$f' < 0$ (negative separation) when

$K/b > 1$ (for nondissociating solutes)

$K/b > 1/(\nu^+ + \nu^-)$ (for strong electrolytes)

and

$f' = 0$ (no separation) when

$K/b = 1$ (for nondissociating solutes)

$K/b = (\nu^+ + \nu^-)$ (for strong electrolytes)

Therefore, this modified model, the MD-FPM, can predict positive, negative, or zero separation, which is consistent with experimental results. For instance, negative separation is found for solutes such as phenol with cellulose acetate membranes.[6]

Equation of Dimensionless Fluid Velocity in FPM

As given in Ref. 3, the volumetric flux of permeation in FPM-3 is

$$J_V = \frac{\epsilon R_W^2}{8\eta} \left[\frac{1}{1 + R_W^2 \chi_{AM} C_{A3}/8\eta} \right] \frac{\Delta P - \Delta\pi(1 - K)}{\tau} \tag{37}$$

and from [1] for FPM-4 is

$$J_V = \frac{\epsilon R_W^2}{8\eta} \left[\frac{1}{1 + R_W^2 \chi_{AM} C_{A3}/8\eta} \right]$$
$$\times \frac{\Delta P - (1 - K_2)\pi_2 + (1 - K_3)\pi_3}{\tau} \tag{38}$$

Then, using eq. (11), eq. (38) can be rearranged in terms of the dimensionless solution velocity as

$$\alpha = (R_W^2/8\eta)(\chi_{AB}/RT)$$
$$\times \frac{[\Delta P - (1 - K_2)\pi_2 + (1 - K_3)\pi_3]}{1 + (R_W^2/8\eta)(\chi_{AB}/RT)(b - 1)C_{A3}RT} \tag{39}$$

Equation (39) can be compared directly to eq. (24) in the MD-FPM model. First, the MD-FPM-4 [eq. (24)] and the FPM-4 [eq. (39)] are similar when the approximation in eq. (23) is valid, although no such restriction exists in the formulation of the FPM. The partition coefficients in eq. (39) are compared to the coefficients divided by the b factor in eq. (24), and the $C_{A3}RT$ term, in eq. (39), is replaced by $\pi_2 K/b$ in eq. (24). These differences may lead to different predictions under special conditions.

The MD-FPM-3 Relationship

The MD-FPM equations discussed so far are for the general case of MD-FPM-4 relationship in which partition coefficients are allowed to vary from the pore inlet to the pore outlet. However, frequently the partition coefficient is assumed to be constant,

$$K_2 = K_3 = K \tag{40}$$

Making this above assumption generates the MD-FPM-3 which is then a three-parameter model. When eq. (40) holds, the MD-FPM-4 equations (22), (24), (29), (35), and (36) reduce to the following forms for the MD-FPM-3 relationship, respectively:

$$\alpha = \frac{R_W^2}{8\eta} \left(\frac{\chi_{AB}}{RT} \right) \left[\Delta P - \Delta\pi(1 - K) - \alpha\left(\frac{K}{b}\right) \right.$$
$$\left. \times (b - 1)\left(\pi_2 + \frac{\Delta\pi}{\exp(\alpha) - 1} \right) \right] \tag{41}$$

$$\alpha = \frac{(R_W^2/8\eta)(\chi_{AB}/RT)[\Delta P - \Delta\pi(1 - K/b)]}{1 + (R_W^2/8\eta)(\chi_{AB}/RT)(K/b)(b - 1)\pi_2} \tag{42}$$

$$N_T = \frac{1}{\chi_{AB}} \left(\frac{\alpha}{\tau/\epsilon} \right) \left\{ \left[\pi_2 + \frac{\Delta\pi}{\exp(\alpha) - 1} \right] \frac{K}{b} \right.$$
$$\left. + CRT\left(\frac{\alpha_B}{\alpha} \right) \right\} \tag{43}$$

$$C_{A3} = C \left(1 + CRT\left(\frac{\alpha_B}{\alpha} \right) \right.$$
$$\left. \times \left\{ \left[\pi_2 + \frac{\Delta\pi}{\exp(\alpha) - 1} \right] \frac{K}{b} \right\}^{-1} \right)^{-1} \tag{44}$$

$$f' = \frac{(1 - K/b)[\exp(\alpha) - 1]}{[\exp(\alpha) - 1] + K/b}$$

for nondissociating solutes

$$= \frac{(1 - (\nu^+ + \nu^-)K/b)[\exp(\alpha) - 1]}{[\exp(\alpha) - 1] + (\nu^+ + \nu^-)K/b} \tag{45}$$

for strong electrolytes

where $\Delta\pi$ is the osmotic pressure difference across the membrane:

$$\Delta\pi = \pi_2 - \pi_3 \qquad (46)$$

The concentration profile inside the membrane, in the MD-FPM-3, is given by eq. (B.5) in Appendix B.

RESULTS AND DISCUSSION

In this section, some of the key results using the new MD-FPM-3 relationship are examined and compared to similar cases for the FPM-3 relationship. Similar results can be obtained using the MD-FPM-4 relationship; however, these results are not shown for the sake of brevity.

Solution to MD-FPM and FPM Relationships

In order to use the MD-FPM model, as outlined in the Theory section, the equations describing the fluid permeation flux and separation are coupled and, therefore, a trial and error technique is required to find the solution. The appropriate equations that need to be solved for the MD-FPM-3 relationship are eqs. (30), (41), and (45). If eq. (23) holds, eq. (42) can be used instead of eq. (41). The Faxen equation is suggested to predict the b factor in the case of solute exclusion from the membrane.[5]

In a simulation it is of interest to examine the direct effect of changing the model parameters on membrane performance. However, for any of the FPM (or MD-FPM) models this procedure is confounded by the interdependence of the model parameters. The partition coefficient K and friction function b are both known to be functions of membrane pore size (e.g., Ref. 5). Increasing the pore size decreases the partition coefficient for two reasons: The potential function between the solute and the pore wall decreases as the solute is further from the membrane, and the size of the solute relative to the pore size decreases which reduces steric exclusion from the pore. Similarly, increasing the pore size reduces b as the hydrodynamic drag between the solute and the pore wall is decreased.

Therefore, a method of quantifying the interdependence of the parameters is required. The relationship between b and pore size can be approximated by the Faxen equation. The relationship between partition coefficient and membrane surface potential can be related by the Boltzmann equation;

this relationship, which is used in 2-dimensional pore models in Refs. 5 and 7, can be written as

$$K(\rho) = \exp[-\Phi(\rho)] \qquad (47)$$

where

$$\rho = r/R_W \qquad (48)$$

so that the K value is

$$K = \int_0^{1-\lambda} K(\rho)\rho\, d\rho \bigg/ \int_0^1 \rho\, d\rho$$
$$= 2 \int_0^{1-\lambda} \exp[-\Phi(\rho)]\rho\, d\rho \qquad (49)$$

where λ is the ratio of solute molecular radius to the pore radius. As suggested in the modified surface force-pore flow (MD-SF-PF) model,[5] an empirical relationship for the potential may be written, for the case of solute exclusion from membranes, as

$$\Phi(\rho) = \begin{cases} (\theta_1/R_W)\exp(\rho^2/2) & \text{when } (1-\rho) > \lambda \\ \infty & \text{when } (1-\rho) \leq \lambda \end{cases} \qquad (50)$$

Equations (49) and (50) establish a reasonable relationship between the membrane pore size and partition coefficient parameters.

To solve the MD-FPM-3 relationship, knowing the parameters of the model (R_W, τ/ϵ, and K or θ_1), the following procedure is recommended:

(1) Make an initial guess for C_{A3}.
(2) Solve eq. (41) to find α. An iterative technique is required to solve eq. (41). If eq. (23) holds, eq. (42) may be used instead as the easier solution.
(3) Solve eq. (45) to find the separation f'.
(4) Solve eq. (30), using eq. (31), to find the total permeation flux N_T.

It has been assumed, in the above procedure, that the Faxen equation is used to predict b,[5] and eqs. (49) and (50) are employed to determine the partition coefficient K as a function of pore size.

A similar procedure can be used to solve the MD-FPM-4 relationship. In this case, the equations to be solved are eqs. (22), (36), (30), and (31). Equation (24) may be used instead of eq. (22) if eq. (23) holds.

For the case of FPM relationships, similar numerical procedure can be taken. Equations (39), (17), (30), and (31) are used to solve the FPM-4 relationship. For the FPM-3 relationship, the same equations are used together with the simplification of eq. (40) to solve the model. Again, the Faxen equation has been assumed to predict b.

Simulation Results

In order to see how the MD-FPM-3 relationship behaves differently from the FPM-3 relationship, the two models were evaluated under a variety of simulated conditions. These results are discussed below.

Separation and Flux Ratio. Figure 2 illustrates the effect of K/b on membrane separation for both the MD-FPM-3 and FPM-3 relationships. The operating conditions are: C_{A2} = 0.04840 and 0.27151 kmol/m^3 of NaCl in water in Figures 2(a) and 2(b), respectively, ΔP = 1500 kPa and T = 25°C; the membrane has a pore radius of 9.39 × 10^{-10} m. For both models, separation increases with decreasing K/b [increasing potential according to eq. (47)]. Calculations are only done for K/b in the range 1.0– 1.0 × 10^{-4} as normally K/b values for NaCl solute would fall in this range. These results are consistent with the limiting cases discussed in the subsection beginning with eq. (25). It should be noted that, since K and b are both functions of pore size, the results in Figure 2 (at a fixed pore size) imply a fixed b value (for the fixed solute NaCl) and a change in membrane potential as K/b changes [see eq. (47)]. What is clear is the two models will predict different separation values for the same K/b parameter; the FPM-3 model overpredicts separation values by up to 90%. Over the whole range, the separation is always predicted to be lower by the MD-FPM model than by the FPM model. This difference is caused by the correct inclusion of solute osmotic pressure by the MD-FPM model and by the inclusion of the diffusional component of the solute flux in the MD-FPM model that is ignored in the FPM model (i.e., the higher the solute flux the lower the separation). In the limit, with a small partition coefficient K or large friction factor b, the FPM and MD-FPM relationships approach each other. Thus for very small pores, where the solute is almost completely rejected the two models both converge to 100% separation as expected. This limit can also be reached when the membrane potential is very strong which results in a very small partition coefficient for the case of solute exclusion from the membrane.
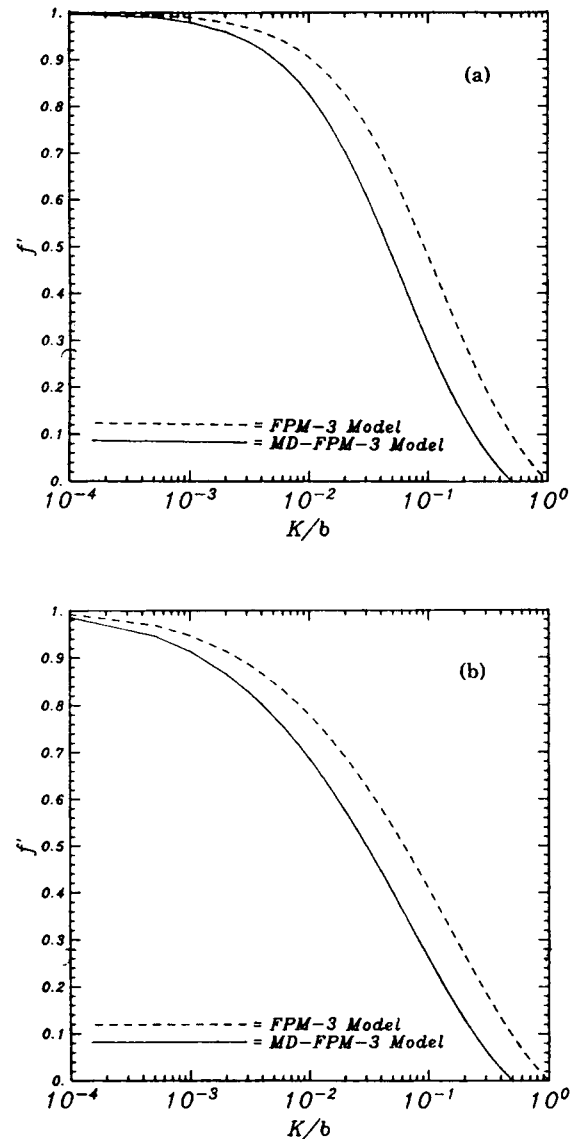

Figure 2 Effect of K/b ratio on membrane separation for the NaCl–H$_2$O system as predicted by the MD-FPM model (—) and FPM model (- - -): (a) C_{A2} = 0.04840 kmol/m^3, (b) C_{A2} = 0.27151 kmol/m^3. Other conditions are: ΔP = 1500 kPa, T = 25°C, and R_W = 9.39 × 10^{-10} m.

Figure 2(b) illustrates similar information for the higher feed concentration of C_{A2} = 0.27151 kmol/ m^3 of NaCl in water, keeping the other conditions same as in Figure 2(a). The same trends, as in Figure 2(a), are predicted except the separation values are lower for this higher concentration case. The lower separation at higher concentration is expected due to the higher osmotic pressures at higher concentrations. Again, the two models approach each other at lower values of K/b and the FPM model

overpredicts the separation values due to the reasons stated above.

Equations (49) and (50) have been employed to study the effect of membrane pore size on membrane performance as illustrated in Figure 3. The operating conditions are: C_{A2} = 0.04840 and 0.27151 kmol/m^3 of NaCl in water, ΔP = 1500 kPa, T = 25°C, and the potential parameter used is θ_1 = 53.73 × 10^{-10} m, which is a typical value for a reverse osmosis membrane. Figure 3(a) illustrates how separation varies with pore size; as the pore size is increased,
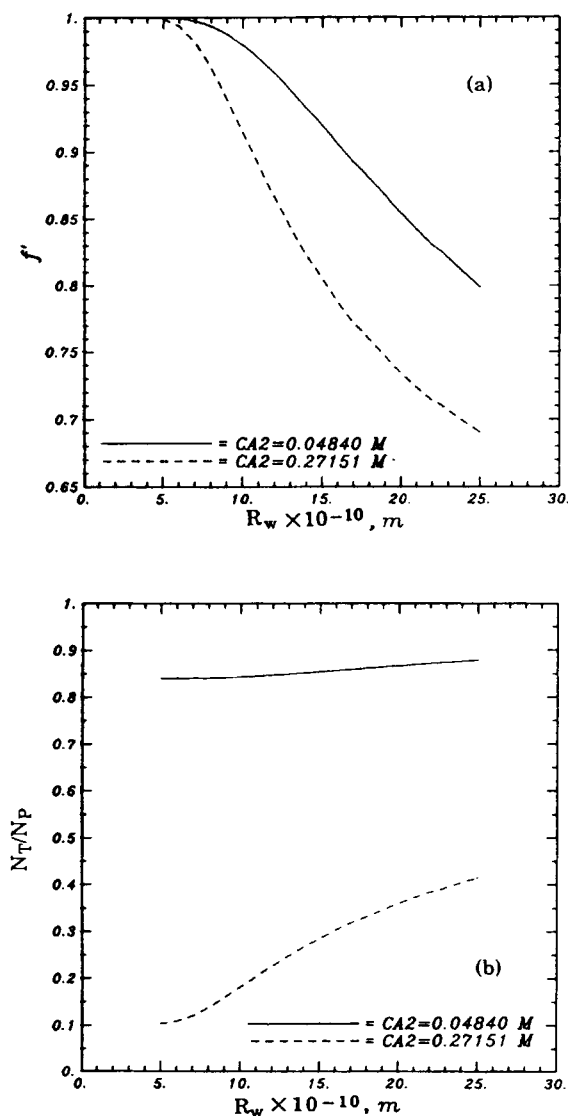
the separation decreases. The decrease in separation is more pronounced for the higher feed concentration (i.e., the dashed line). These results are consistent with those in the literature.[8] The flux ratio is the ratio of the solution flux with solute present to the flux of pure water. Figure 3(b) illustrates how the flux ratio N_T/N_P varies under the same conditions as in Figure 3(a). As the pore size is increased the flux ratio increases toward unity, and as the feed concentration is increased the ratio decreases due to osmotic pressure effects.

Figure 4 presents typical results for reverse osmosis membrane performance for the usual case of solute exclusion. Figure 4(a) investigates the multiple effects of operating pressure ΔP and membrane pore size R_W on the separation f' and the flux ratio N_T/N_P by the MD-FPM-3 relationship. The feed concentration is C_{A2} = 0.04840 kmol/m^3 of NaCl in water, and T = 25°C. The membrane potential parameters are the same as in Figure 3. As the operating pressure is increased, the separation and flux ratio increase, and as the pore size is increased the separation decreases and the flux ratio increases. These are expected trends as observed experimentally and are similar to those predicted by the MD-SF-PF model.[5]

Concentration Profiles. This section considers the concentration profiles through the membrane as predicted by the MD-FPM-3 and FPM-3 relationships. The concentration profiles are given by eq. (B.5) (MD-FPM-3 relationship) and eq. (B.9) (FPM-3 relationship). In the MD-FPM model, since the differential equation for solute concentration is restricted to boundary values at the two end points of the membrane, negative concentrations are never predicted. However, in the FPM model, because the differential equation in this model is restricted to only one end point of the membrane and the other end point is free, negative values for solute concentration can be predicted which is physically unrealistic.

To compare the two models in this respect, one set of experimental data from Jonsson and Boesen[3] are examined as follows. Choosing the DDS-800 membrane and 1% sucrose-water system, the data are: C_{A2} = 0.03 kmol/m^3, C_{A2}/C_{A3} = 1.3444, and J_V = 1.0 × 10^{-4} m/s. Using the FPM-3 relationship, they estimated[3]

Figure 3 Effect of membrane pore size, with feed concentration as a parameter, on membrane performance for the NaCl–H$_2$O system as predicted by the MD-FPM model: (a) separation vs. pore size; (b) flux ratio vs. pore size. Conditions: ΔP = 1500 kPa, T = 25°C, and θ_1 = 53.73 × 10^{-10} m.

$$R_W = 15 \times 10^{-10} \text{ m}, \qquad \tau/\epsilon = 29.5 \times 10^{-6} \text{ m},$$

$$K = 0.76, \qquad \text{and} \qquad b = 1.362$$

The above data are used, now, in the equations of concentration profiles. The diffusivity data for sucrose systems are given in Table 5.2-1 of Ref. 9; for a $0.03 M$ aqueous solution the value is $D_{AB} = 0.515 \times 10^{-9}$ m^2/s. Equations to determine α are eq. (41) in MD-FPM-3 and eqs. (39) and (40) in FPM-3.

The results are shown in Figures 5(a) and 5(b) for the MD-FPM-3 and FPM-3 relationships, respectively. The MD-FPM-3 relationship predicts reasonable values that satisfy the boundary conditions. However, the FPM-3 relationship predicts
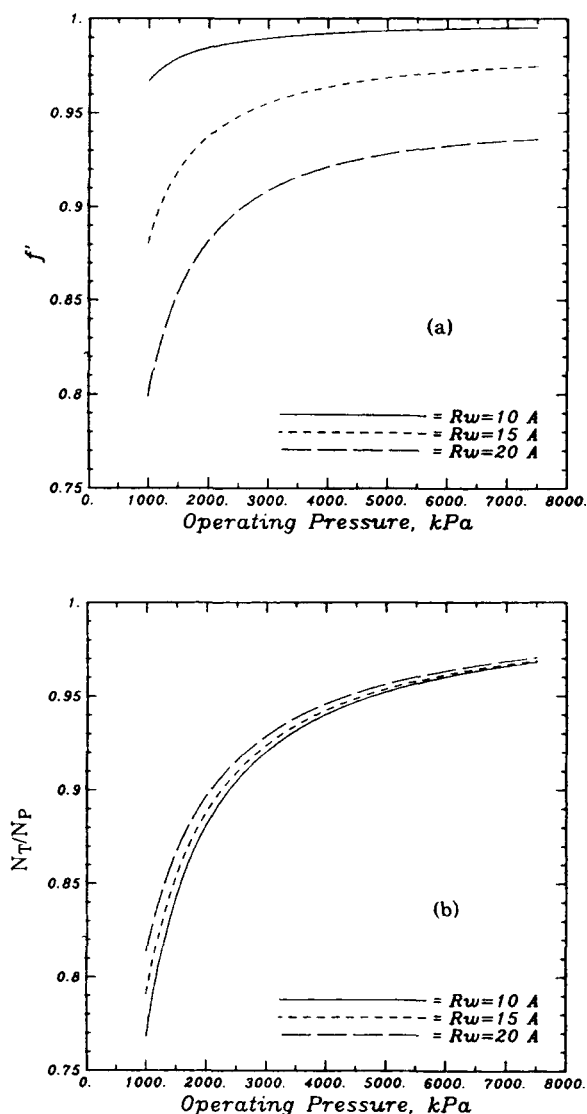
Figure 4   Effect of operating pressure, with pore size as a parameter, on membrane performance for the NaCl–H$_2$O system as predicted by the MD–FPM model: (a) separation vs. pressure; (b) flux ratio vs. pressure. Conditions: $C_{A2} = 0.04840$ kmol/m^3, $T = 25°$C, and $\theta_1 = 53.73 \times 10^{-10}$ m.
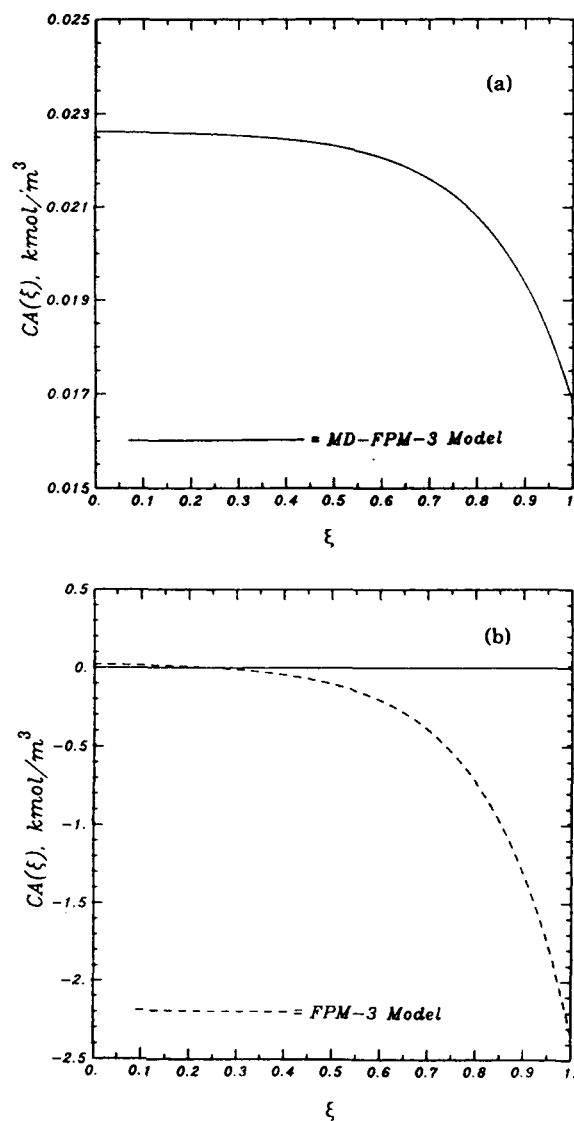
Figure 5   Concentration profile inside the pore for sucrose-water system as predicted by: (a) MD-FPM model; (b) FPM model. Conditions[3]: feed concentration = 1% sucrose ($C_{A2} = 0.03$ kmol/m^3), $C_{A2}/C_{A3} = 1.3444, K = 0.76$, $R_W = 15 \times 10^{-10}$ m, $b = 1.362$, and $\tau/\epsilon = 2.95 \times 10^{-5}$ m.

negative values for the concentration after $\xi > 0.2385$ inside the pore so that the boundary condition at $\xi = 1$ is not satisfied. Obviously, this situation is impossible. This result is a reflection of the incorrect form of the material balance used in the derivation of the FPM relationships as discussed in the first subsection of the Theory section. Therefore, the concentration gradient, which drives the solute through the membrane, is calculated incorrectly for the FPM model and hence the membrane performance is also incorrectly calculated.

CONCLUSIONS

The finely porous model (FPM) has been modified and extended, mathematically, in several key respects. The extended model, called the modified finely porous model (MD-FPM) has been derived, in detail, with either three or four adjustable parameters; the MD-FPM-3 and MD-FPM-4 relationships, respectively. The differences include the material balance on the solute in the pore, the fluid velocity in the pore, and correction of osmotic effects for the case of electrolytes. An efficient procedure is presented to solve the models. The new model has been shown to predict the performance expected for reverse osmosis membranes. The differences between the FPM and MD-FPM relationships have been illustrated as functions of operating variables. The models are further compared by using data in the literature for aqueous sucrose solutions and a DDS membrane. The FPM relationship can predict unreasonable results for the concentration profile in the membrane while the concentration profile is correctly predicted by the MD-FPM relationship.

NOMENCLATURE

b	friction parameter defined in eq. (3), dimensionless
C	molar density of solution ($kmol/m^3$)
C_{A2}	solute concentration at boundary-layer solution ($kmol/m^3$)
C_{A3}	solute concentration in permeate solution ($kmol/m^3$)
$C_A(z)$	axial solute concentration inside a pore ($kmol/m^3$)
D_{AB}	solute diffusivity in free solution (m^2/s)
D_{AM}	solute diffusivity inside a pore (m^2/s)
f'	theoretical separation defined by eq. (16), dimensionless
F_A	total force driving solute through the pore ($kJ/m\ kmol$)
F_{AB}	frictional force between solute and solvent ($kJ/m\ kmol$)
F_{AM}	frictional force between solute and the pore wall ($kJ/m\ kmol$)
g	constant of integration in eq. (B.7) ($kmol/m^3$)
G	constant of integration in eq. (B.1) ($kmol/m^3$)
H	constant of integration in eq. (B.3) ($kmol/m^3$)
$I(\xi)$	integrating factor defined by eq. (B.2), dimensionless
J_A	solute flux through a single pore ($kmol/m^2\ s$)
J_B	solvent flux through a single pore ($kmol/m^2\ s$)
J_V	volumetric flux through a membrane ($m^3/m^2\ s$)
$K(\rho)$	local partition coefficient, dimensionless
K_2	partition coefficient defined in eq. (5), dimensionless

K_3	partition coefficient defined in eq. (6), dimensionless
N_A	solute flux through a membrane ($kmol/m^2\ s$)
N_B	solvent flux through a membrane ($kmol/m^2\ s$)
N_T	total permeation flux through a membrane ($kmol/m^2\ s$)
ΔP	hydrostatic pressure (kPa)
r	radial coordinate inside the pore and normal to axial flow (m)
R	gas constant ($kJ/kmol\ K$)
R_A	effective radius of solute molecule (m)
R_W	average radius of membrane pores (m)
T	temperature (K)
u	solution velocity inside the pore (m/s)
u_A	solute velocity inside a pore (m/s)
u_B	solvent velocity inside a pore (m/s)
z	cylindrical coordinate parallel to the pore wall (m)

Greek Letters

α	solution velocity defined in eq. (11), dimensionless
α_B	solvent velocity defined in eq. (A.9), dimensionless
ϵ	fractional pore area of membrane, dimensionless
η	solution viscosity (kPa s)
θ_1	potential parameter defined in eq. (50) (m)
λ	ratio of solute molecular radius to pore radius, dimensionless
μ_A	chemical potential of solute in the pore ($kJ/kmol$)
ν^+	number of kmol of cations from dissociation of 1 kmol salt
ν^-	number of kmol of anions from dissociation of 1 kmol salt
ξ	axial coordinate defined in eq. (12), dimensionless
π_2	osmotic pressure of boundary-layer solution (kPa)
π_3	osmotic pressure of permeate (kPa)
$\pi(z)$	osmotic pressure of solution inside the pore (kPa)
$\Delta\pi$	osmotic pressure difference defined by eq. (46) (kPa)
ρ	radial coordinate defined in eq. (48), dimensionless
τ	average pore length taking tortuosity into account (m)
$\Phi(\rho)$	potential function defined by eq. (50), dimensionless
χ_{AB}	friction constant between solute and solvent ($kJ\ s/m^2\ kmol$)
χ_{AM}	average friction constant between solute and membrane ($kJ\ s/m^2\ kmol$)

APPENDIX A: DERIVATION OF SOLUTE FLUX EQUATIONS IN THE FPM AND MD-FPM RELATIONSHIPS

A balance of applied and frictional forces on the solute molecules in the pore yields[3]

$$F_A = (F_{AB} + F_{AM}) \tag{A.1}$$

where

$$F_{AM} = -\chi_{AM} u_A = -\chi_{AM} J_A / C_A(z) \quad (A.2)$$

and

$$F_{AB} = -\chi_{AB}(u_A - u_B)$$
$$= -\chi_{AB}[J_A / C_A(z) - u_B] \quad (A.3)$$

The driving force for the solute, F_A, is[5]

$$F_A = -\frac{d\mu_A(z)}{dz} = -\frac{RT}{\pi(z)}\frac{d\pi(z)}{dz} \quad (A.4)$$

Then, eq. (A.1), using eqs. (A.2) and (A.4), becomes

$$-F_{AB} = (F_A + F_{AM})$$
$$= -\frac{RT}{\pi(z)}\frac{d\pi(z)}{dz} - \chi_{AM}\frac{J_A}{\pi(z)}RT \quad (A.5)$$

On the other hand, from eq. (A.3),

$$J_A = \frac{1}{\chi_{AB}}\frac{\pi(z)}{RT}[-F_{AB}] + \frac{\pi(z)}{RT}u_B \quad (A.6)$$

Now, using eq. (A.5), eq. (A.6) becomes

$$J_A = \frac{1}{b}\left[-\frac{1}{\chi_{AB}}\frac{d\pi(z)}{dz} + \frac{\pi(z)u_B}{RT}\right] \quad (A.7)$$

where b has been defined by eq. (3). Equation (A.7) can be rewritten as

$$J_A = \frac{1}{b}\left(\frac{1}{\tau\chi_{AB}}\right)\left[-\frac{d\pi(\xi)}{d\xi} + \alpha_B\pi(z)\right] \quad (A.8)$$

where ξ has been defined by eq. (12) and

$$\alpha_B = \frac{u_B\tau\chi_{AB}}{RT} \quad (A.9)$$

Now, using eq. (13) and van 't Hoff's law of osmotic pressure,[5]

$$\pi(\xi) = \left\{\pi_2 - \left(\pi_2 - \frac{K_3}{K_2}\pi_3\right)\right.$$
$$\left.\times\left[\frac{1 - \exp(\alpha\xi)}{1 - \exp(\alpha)}\right]\right\}K_2 \quad (A.10)$$

The derivative $d\pi/dz$ can be determined from the above equation. Using this derivative and eq. (A.10), eq. (A.8) becomes

$$J_A = \frac{\alpha}{\tau\chi_{AB}b}\left[\pi_2 + \frac{\pi_2 - (K_3/K_2)\pi_3}{\exp(\alpha) - 1}\right]K_2 \quad (A.11)$$

which is the equation of solute flux in MD-FPM-4 relationship.

Employing eq. (40), the above equation reduces to the following form for the MD-FPM-3 relationship:

$$J_A = \frac{\alpha}{\tau\chi_{AB}b}\left[\pi_2 + \frac{\pi_2 - \pi_3}{\exp(\alpha) - 1}\right]K \quad (A.12)$$

APPENDIX B: DERIVATION OF CONCENTRATION PROFILES AND SEPARATION IN THE MD-FPM AND FPM RELATIONSHIPS

MD-FPM Relationship

Starting with eq. (9) and the boundary conditions, eqs. (5) and (6), eq. (9) is integrated with respect to ξ to yield

$$\frac{dC_A(\xi)}{d\xi} - \alpha C_A(\xi) = -\alpha G \quad (B.1)$$

where G is a constant of integration. Multiplying eq. (B.1) by the following integration factor,

$$I(\xi) = \exp(-\alpha\xi) \quad (B.2)$$

and integrating the resulted equation, one obtains

$$C_A(\xi) = G + H\exp(\alpha\xi) \quad (B.3)$$

where H is another constant of integration.

In order to determine the constants G and H, the boundary conditions are employed. Using eqs. (5) and (6), G and H are determined and substituted into eq. (B.3) to give the concentration profile in MD-FPM-4 relationship as

$$C_A(\xi) = \left\{C_{A2} - \left(C_{A2} - \frac{K_3}{K_2}C_{A3}\right)\right.$$
$$\left.\times\left[\frac{1 - \exp(\alpha\xi)}{1 - \exp(\alpha)}\right]\right\}K_2 \quad (B.4)$$

Using eq. (40), the above equation reduces, for the MD-FPM-3 relationship, to the following form:

$$C_A(\xi)$$
$$= \left\{ C_{A2} - (C_{A2} - C_{A3}) \left[\frac{1 - \exp(\alpha\xi)}{1 - \exp(\alpha)} \right] \right\} K \quad \text{(B.5)}$$

FPM Relationship

Combining eqs. (1) and (15), the following first-order differential equation is obtained:

$$\frac{dC_A(\xi)}{d\xi} - \alpha C_A(\xi) = -\alpha C_{A3} \quad \text{(B.6)}$$

where α and ξ have been defined by eqs. (11) and (12). Multiplying eq. (B.6) by the integrating factor in eq. (B.2) and integrating the resulted equation, one obtains

$$C_A(\xi) = C_{A3} b + g \exp(\alpha\xi) \quad \text{(B.7)}$$

Using eq. (5) as the boundary condition, the constant g is determined and substituted into eq. (B.7) to give the concentration profile in FPM-4 relationship as

$$C_A(\xi) = b \left[C_{A3} + \left(\frac{K_2}{b} C_{A2} - C_{A3} \right) \exp(\alpha\xi) \right] \quad \text{(B.8)}$$

Equation (40) can be employed to convert the above equation to the concentration profile in FPM-3 as

$$C_A(\xi) = b \left[C_{A3} + \left(\frac{K}{b} C_{A2} - C_{A3} \right) \exp(\alpha\xi) \right] \quad \text{(B.9)}$$

Now, using eq. (6), eq. (B.8) can be employed to derive the following relationship for the C_{A3}/C_{A2} ratio:

$$\frac{C_{A3}}{C_{A2}} = \frac{(K_2/K_3)\exp(\alpha)}{1 + (b/K_3)[\exp(\alpha) - 1]} \quad \text{(B.10)}$$

Then, using eq. (16) as the definition of separation, the following correlations are derived for separation, in the FPM-4 relationship:

$$f' = \frac{(1 - K_2/b)\exp(\alpha) - (1 - K_3/b)}{[\exp(\alpha) - 1] + K_3/b} \quad \text{(B.11)}$$

which reduces to the following form for FPM-3 relationship, when eq. (40) is employed:

$$f' = \frac{(1 - K/b)[\exp(\alpha) - 1]}{[\exp(\alpha) - 1] + K/b} \quad \text{(B.12)}$$

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