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Nanofiltration of uncharged solutes: simultaneous effect of the polarization and membrane layers on separation

Endre Nagy

FIT, Research Institute of Chemical and Process Engineering, University of Pannonia, Veszprém, Hungary
Tel. +36 88 624040; Fax: +36 88 624038; email: nagy@mukki.richem.hu

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ABSTRACT

The effect of the concentration boundary layer on the pressure-driven membrane separation like nanofiltration or ultrafiltration is well-known and extensively discussed in the literature. In most of these studies, the effect of the boundary layer and that of the membrane layer on the separation efficiency are discussed separately. This paper presents a general model to describe the convective and diffusive mass transport taking into account the simultaneous effect of both the concentration boundary layer and the membrane layer. The advantage of this model that the mass transport can be correctly described under all mass transfer conditions, independently that the effect of the boundary layer can or not be neglected.

Keywords: Nanofiltration; Simultaneous effect of polarization and membrane layer; Hindered diffusion; Mass transefer; Diffusion plus convection; Concentration polarization; Polarization modulus; Rejection coefficient

1. Introduction

The mass transport of uncharged solute molecules like submicron or nanometer sized particles, colloids, etc., their size, the steric (sieving) effects causing hindered diffusion and convection in the membrane matrix, the porosity, thickness and other membrane properties, etc. may have essential influence on the separation that can be achieved [1–5] during pressure-driven separation processes such as ultrafiltration, reverse osmosis or nanofiltration. Then, this transport can be significantly affected by the formation of a concentration polarization layer on the feed side of the membrane [6,7]. How these two mass transport layers influence, simultaneously, the separation efficiency as a function of their mass transport parameters is discussed in this paper.

Concentration polarization can be governed by solute properties, membrane properties, and hydrodynamics [6]. A number of papers have analyzed the effect of the concentration polarization, and defined the well-known equations to predict it [6–9]. These studies, applying the film model [6–7], consider the mass transport in the boundary layer only, defining its Peclet number ($Pe_L = \upsilon_o \delta / D_o$), but do not discuss that in the membrane layer, its effect back on the concentration polarization layer and on separation. In principle, the velocity profile can be obtained by completely solving the Navier-Stokes and the continuity equations [10]. The two-dimensional models involve the transverse velocity function in the axial direction, driving force, permeate flux, wall concentration, wall Peclet number, rejection coefficient, etc. but they do not give information on how the membrane properties can influence directly the mass transfer resistance of the polarization layer and the permeate concentration, and, thus, the separation. They describe the solute concentration within the concentration polarization layer while the concentration is not analyzed in the membrane layer.

Other researchers have investigated the effect of the membrane properties on the mass transport during traditional nanofiltration [1–4]. The diffusive and the

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convective transport of species through the membrane pores or through a porous polymer network can be expressed by hindrance factors developed by Deen [1] and Bowen et al. [2,3]. They define a mathematical equation to predict the rejection coefficient as a function of the membrane properties such as pore size, permeate flux, membrane diffusion coefficient, membrane thickness, porosity, etc. But this model neglects the effect of the concentration polarization layer assuming that the boundary layer's Peclet number is close to zero, and, consequently, it is negligible.

The aim of this paper is to develop mathematical equations that enable the user to predict the simultaneous effect of the concentration polarization and the membrane layers on the mass transport taking into account the membrane properties as well. For this, the well-known one-dimensional film theory with diffusive and convective mass transfer for the concentration polarization layer is applied.

2. Theory

The sum of the diffusive and the convective mass transport, denoted by *J*, related to the total membrane interface, can be given by the well-known expression, for example for the concentration polarization layer, as follows [3,7]:

$$J = \upsilon_o C - D_o \frac{dC}{dy} \tag{1}$$

During filtration processes, the uncharged solute particles (macromolecules, submicron- or nanometer sized particles, colloids, etc.), their size, the steric (sieving) effects may have essential influence on the separation efficiency [1–4]. Due to the steric effects, a hindered diffusion and convection can take place in the membrane matrix. Accordingly, the specific, overall mass transfer rate, through a membrane matrix, can be defined, in relation to the total membrane interface, as follows [3]:

$$J = \alpha \upsilon_o C - D_m \frac{dC}{dy} \tag{2}$$

where

$$\alpha = \xi_c - \frac{D_m V}{RT} \frac{8\eta}{r_p^2} \tag{3}$$

and

$$D_m = D_o \xi_d \frac{\varepsilon}{\psi\tau} \tag{4}$$

where $\psi = \frac{\eta}{\eta_o}$

The ξ_d and ξ_c parameters are related to the hydrodynamic coefficient and the lag coefficient of the spherical solute moving inside a cylindrical pore of infinite length [1,3,4]. Deen [1] reviewed various equations that were used to predict the value of the hindrance factors. The second additional term of Eq. (3) involves the effect of pressure on the chemical potential [3]. At relatively low pressures, this term can be neglected; as it is mostly the case for nanofiltration [3], and accordingly $\alpha = \xi_c$.

The convective permeation flow can be given by the well known Hagen-Poiseuille relationship [3,6,7]:

$$\upsilon_o = \frac{r_p^2 \left(\Delta P - \Delta\pi\right) \varepsilon}{8\eta\delta_m\tau} \equiv \frac{r_p^2 \left(\Delta P - \Delta\pi\right)}{8\eta_o} \frac{1}{N} \tag{5}$$

with

$$N = \frac{\psi\delta_m\tau}{\varepsilon} \tag{6}$$

The viscosity, η, in Eq. (5) denotes its real value that can be much higher, in the narrow pore of the membrane than its bulk value ($\eta=\eta_o\{1+18d/r_p-9(d/r_p)^2$; for water $d = 0.28$ nm, [3,12]}.

The integration of Eqs. (1) and (2), the concentration distribution of the boundary layer and the membrane layer can be given (applying dimensionless space coordinate, $Y = y/\delta$), as follows [6,11]:

For the boundary layer:

$$C = T_L e^{Pe_L Y} + Q_L \tag{7}$$

For the membrane layer:

$$C = T_m e^{Pe_m} + Q_m \tag{8}$$

where $Pe_L = \frac{\upsilon_o\delta}{D_o} \equiv \frac{\upsilon_o}{k_L}$; $\quad Pe_m = \frac{\upsilon_o\delta_m\alpha}{D_m} \equiv \frac{\upsilon_o}{k_m}\alpha$

Substituting the value of υ_o from Eq. (5) as the D_m value from Eq. (4) into the expression of the above Pe_m, the Peclet number of the membrane can be expressed as follows:

$$Pe_m = \frac{r_p^2 \left(\Delta P - \Delta\pi\right)}{8 D_o \eta_o} \frac{\alpha}{\xi_d} \tag{9}$$

Note that regarding the membrane structure, Eq. (9) does not involve the $\delta_m\tau\psi/\varepsilon$ parameter but the pore radius only. Accordingly, if the pore radius is known, the diffusion membrane mass transfer coefficient can be predicted by means of Pe_m, namely according to Eq. (8) one can get:

$$k_m = \frac{\upsilon_o \alpha}{Pe_m} \tag{10}$$

or applying Eq. (4) one can obtain:

$$k_m = D_o \xi_d \frac{\varepsilon}{\tau \delta_m \psi} \equiv D_o \xi_d \frac{1}{N} \tag{11}$$

Eqs. (10) and (11) should give the same results, thus parameter N ($N = \delta_m \tau\psi/\varepsilon$) can be calculated for example by the following equation, as well [similarly, this parameter can easily be predicted by Eq. (5), as well]:

$$N = \frac{D_o \xi_d Pe_m}{\upsilon_o \alpha} \tag{12}$$

Values of T_L, Q_L and T_m, Q_m parameters in Eqs. (7) and (8) can separately be determined by general boundary conditions as follows:

For the polarization layer:

$$T_L + Q_L = C_b \qquad \text{at} \quad Y = 0 \tag{13}$$

$$\left(T_L e^{Pe_L} + Q_L\right) = C^* \qquad \text{at} \quad Y = 1 \tag{14}$$

Thus, one can obtain for T_L and Q_L as follows:

$$T_L = \frac{C_b - C^*}{1 - e^{Pe_L}} \tag{15}$$

and

$$Q_L = \frac{C^* - C_b e^{Pe_L}}{1 - e^{Pe_L}} \tag{16}$$

For the membrane layer:

$$T_m + Q_m = C_m^* \qquad \text{at} \quad Y = 0 \tag{17}$$

$$T_m e^{Pe_m} + Q_m = C_{m\delta} \qquad \text{at} \quad Y = 1 \tag{18}$$

The T_m and Q_m can similarly be obtained by means of Eqs. (17) and (18). Then the mass transfer rate for the both of the layers can be expressed as follows:

For the polarization layer:

$$J = Q_L \upsilon_o = \upsilon_o \frac{C^* - C_b e^{Pe_L}}{1 - e^{Pe_L}} \tag{19}$$

as well as for the membrane layer:

$$J = \alpha \frac{C_{m\delta} - C^* e^{Pe_m}}{1 - e^{Pe_m}} \tag{20}$$

By means of Eqs. (19) and (20) the value of J can be expressed by concentrations on the two sides of the layers, namely C_b and $C_{m\delta}$ ($C_{m\delta} = \Phi C_p$). Now accepting that permeate rate, J, is equal to $\upsilon_o C_p$, ($J = \upsilon_o C_p$), the outlet concentration can be expressed as:

$$C_p = \frac{\Phi\alpha C_b e^{Pe_L + Pe_m}}{\left(1 - e^{Pe_m}\right)\left(\Phi\alpha - 1\right) + \Phi\alpha^{Pe_L + Pe_m}} \tag{21}$$

Accordingly the rejection coefficient

$$R \equiv 1 - \frac{C_p}{C_b} = \frac{(\Phi\alpha - 1)(1 - \mathrm{e}^{Pe_m})}{\left(\Phi\alpha - 1\right)(1 - e^{Pe_m}) + \Phi\alpha \mathrm{e}^{Pe_m(1 + k_m/[k\alpha])}} \tag{22}$$

Eq. (22) involves the coupled effect of the concentration polarization and membrane layer. As limiting case, namely if the effect of the concentration polarization layer can be neglected (if $Pe_L \to 0$), Eq. (22) tends to that of the literature equation [3]:

$$\text{If} \quad Pe_L \to 0 \quad \text{then} \qquad \frac{C_p}{C_b} = \frac{\Phi\alpha e^{Pe_m}}{\Phi\alpha - 1 + e^{Pe_m}} \tag{23}$$

3. Results and discussion

The mathematical model developed enables us to calculate the concentration distribution, and thus, the separation performance as a function of the mass transport parameters, e.g. convective velocity, diffusive mass transfer coefficient of the both phases. In order to know these parameters, the permeation rate, $\upsilon_{o,}$ as a function of the transmembrane pressure difference, ΔP–$\Delta\pi$, and the rejection coefficient or the average pore size, r_p, should be measured, and the diffusion coefficients in the layers, molecule size as well as the liquid side mass transfer coefficient should also be predicted.

A typical figure illustrates the value of the rejection coefficient as a function of the membrane's Peclet number in Fig. 1. Value of α and Φ can be regarded as typical values, considering e.g. the separation of glycerol, glucose, lactose or ribose [12]. With the increase of the permeation rate, namely of the Pe_m the R value tends to a maximum value depending strongly on the k_m/k ratio. If concentration polarization does not exist, namely $k_m/k \to 0$, the R rejection coefficient has limiting value. It is clearly shows the strong effect of the polarization layer with

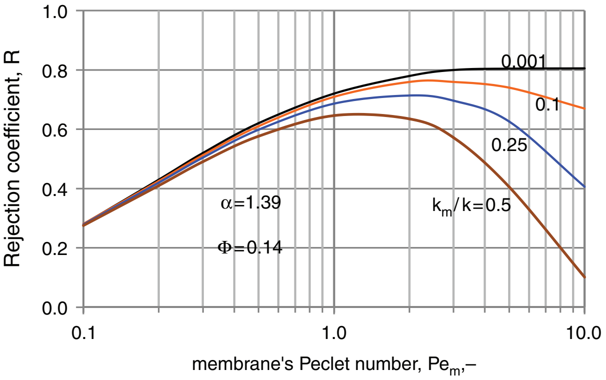

Fig. 1. Typical curves of rejection as a function of Pe_m ($\alpha = 1.39$; $\Phi = 0.14$).

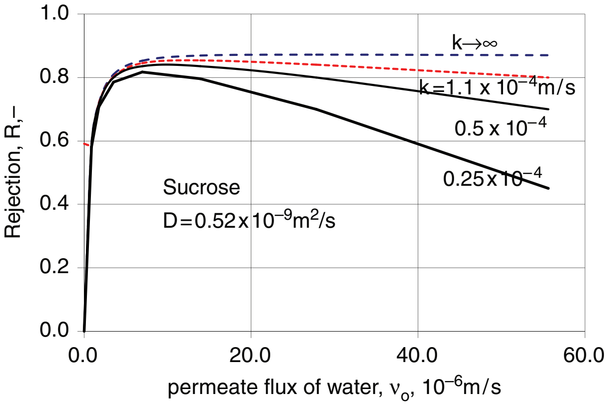

Fig. 2. Nanofiltration of sucrose through MPT 36 membrane [2] in presence of increasing mass transfer resistance of the boundary layer ($\upsilon_o = 55.6 \times 10^{-6}$ m/s at $\Delta P = 3.03$ MPa; $r_p = 0.69$ nm; $R_{\text{measured}} = 0.7$, $r_s = 0.49$ nm).

increasing value of k_m/k. The real value of k_m/k can easily be increased up to 0.1–0.4.

The effect of the permeation rate strongly affects the rejection. Larger transmembrane pressure difference causes larger convective velocity and, thus decreasing rejection depending on the mass transfer resistance of the boundary layer (Fig. 2). The data used for the calculation were taken from paper of Bowen and Mohammad [2] who investigated, among other components, the separation of cucrose.

3.1. Case study

We recalculate certain literature data and compare the rejection results without and with concentration polarization layers. Data used for calculation is taken from papers of Bowen and Welfoot [3]. They measured the separation of glycerol applying a Desal-DK spiral-wound nanofiltration module (Fig. 3 in [3]). The osmotic effect on the permeate flux could be neglected during our calculations due to the low solute concentrations, thus, $\Delta\pi \approx 0$. The second term of the right side of Eq. (3) can also be neglected, as it was stated by Bowen and Welfoot [3] under the conditions of measurements, thus $\xi_c = \alpha$ was used in our calculations.

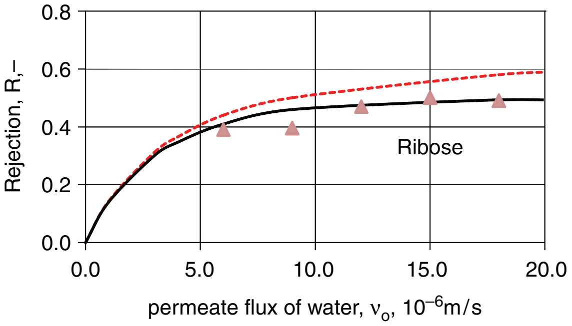

Fig. 3. Comparison of the agreement between experimental (symbols) [3] and adjusted calculated data (dotted lines: without mass transfer resistance in the boundary layer, $Pe_L = 0$; continuous lines: with the effect of the polarization layer); $k_m/(k\alpha) = 0.45$ for glycerol; $r_p = 0.425 \times 10^{-9}$ m.

Let us compare the measured and the predicted data plotted in Fig. 3. The pore size, r_p, was adjusted according to the measured rejection coefficient, R. The r_p value differs slightly from that of the literature (e.g. $r_p = 0.425 \times 10^{-9}$ m in our prediction, while $r_p = 0.45 \times 10^{-9}$ m in the paper of Bowen and Welfoot [3]). The reason is for this discrepancy is that our predicted data is fitted taking into account the effect of the concentration boundary layer on the separation as well (continuous lines). Then, the separation was recalculated neglecting the effect of the boundary layer with $r_p = 0.425 \times 10^{-9}$ m (dotted lines). The value of the $k_m/(k\alpha)$ should be predicted in order to take into account the real effect of the boundary layer's mass transfer resistance as well. The k_m mass transfer coefficient can be estimated by Eq. (10) or Eqs. (11) and (12), while the α can easily be predicted by Eq. (3). As it was mentioned earlier $\alpha \approx \xi_c$. As Baker states [6, p. 175], the boundary layer thickness is about 10–15 µm at a fluid velocity of 0.3 m/s. Let us assume that the boundary layer thickness is about 15 µm yielding high k value and, consequently low value of $k_m/(k\alpha)$. When the real value of k will be lower, obviously the effect of the concentration polarization layer will also increase. Accordingly, $k = 6.3 \times 10^{-5}$ m/s was obtained for glycerol. The $k_m/(k\alpha)$ parameter values obtained are 0.45 for glycerol. As can be seen in Fig. 3, the effect of the concentration polarization lowers the rejection coefficient. Detailed analysis of the above separation is given by Nagy et al. [12].

4. Conclusion

A new mathematical model was developed in order to take into account the simultaneous effect of both the polarization and the membrane layer on separation in pressure-driven membrane processes. This model enables the user to predict the separation efficiency, i.e. the rejection coefficient, the polarization modulus and even the concentration distribution under any operating conditions of nanofiltration or ultrafiltration. Comparing the measured and calculated data, it was shown that the boundary layer's Peclet number can be neglected only when value of the $k_m(k\alpha)$ value can be kept close to zero. This assumption cannot easily be fulfilled when applying a very thin and high-porosity separation layer for nanofiltration.

Symbols

C — concentration, mol/m^3
D — diffusion coefficient, m^2/s
D_o — solute diffusivity in the bulk solvent, m^2/s
J — convective +diffusive mass transfer rate, mol/m^{2}s
k — diffusive mass transfer coefficient; that is for the boundary layer, $(=D_o/\delta)$
k_m — membrane diffusive mass transfer coefficient, m/s
N — constant defined in Eqs. (6) or (10)
P — pressure, Pa
Pe_L — Peclet number of boundary layer related to the membrane area $(=\upsilon_o/k)$
Pe_m — Peclet number for the membrane $(= \upsilon_o \delta_m \alpha \;/\; D_m)$
r_s — radius of solute molecules, m
r_p — effective pore radius, m
R — gas constant, (=8.314 J/molK)
R — rejection coefficient, [Eq. (22)]
T — temperature, K
V — partial molar volume of solute, m^3/mol
y — space co-ordinate perpendicular to the membrane interface, m
Y — dimensionless space coordinate, $(=y/\delta)$

Greek letters

α — parameter defied by Eq. (3)
δ — layer thickness; thickness of the boundary layer, m
ΔP — transmembrane pressure, Pa
$\Delta\pi$ — osmotic pressure difference, Pa
ε — membrane porosity,-
Φ — steric partition coefficient, $(\Phi=[1-\lambda]^2)$
η — solvent viscosity within pores, $(=\eta_o\psi)$, Pas
η_o — bulk solvent viscosity, Pas
λ — ratio of solute to pore radius, $(=r_s/r_p)$
υ_o — solvent velocity in pores related to membrane area, m/s
τ — tortuosity of the membrane
ξ_c — hindrance factor for convection, $(=\{2-\Phi\}(1+0.054\lambda-0.988\lambda^2+0.44\lambda^3\,)$
ξ_d — hindrance factor for diffusion, $(=1-2.3\lambda+1.154\lambda^2+0.224\lambda^3)$
ψ — ratio of pore and bulk solvent viscosity, $(=\eta/\eta_o)$

Subscripts

b — inlet
L — boundary layer
m — membrane or membrane feed side interface
$m\delta$ — membrane permeate side interface
p — permeate

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