Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Bhattacharjee, Chiranjib and Datta, Siddhartha(1996) 'Prediction of Rejection in Ultrafiltration of Macromolecular Solutes', Separation Science and Technology, 31: 1, 95 — 105

To link to this Article: DOI: 10.1080/01496399608000683

URL: http://dx.doi.org/10.1080/01496399608000683

SEPARATION SCIENCE AND TECHNOLOGY, 31(1), pp. 95–105, 1996

Prediction of Rejection in Ultrafiltration of Macromolecular Solutes

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ABSTRACT

A mathematical model based on steady-state mass balance over a boundary layer, coupled with the results from irreversible thermodynamics, is proposed in the present study for ultrafiltration of PEG-6000 using a cellulose acetate membrane. The model is capable of predicting both the membrane surface concentration and permeate concentration, and can be utilized to predict the value of rejection at any operating condition. Three parameters (solvent permeability, solute permeability, and reflection coefficient) were taken into account while developing this model. These parameters, along with the known values of operating conditions and solution properties, allow prediction of rejection. The computed results are in good agreement with the previously published experimental data of Bhattacharjee and Bhattacharya.

INTRODUCTION

Despite the fact that the term "ultrafiltration" first appeared in colloid literature toward the end of the last century, the emergence of ultrafiltration as a viable and practical separation process had its origin with the development of the first synthetic, high hydraulic permeability macromolecule retentive ultrafiltration membrane in 1963. This development was a revolutionary consequence of the asymetric cellulose acetate reverse osmosis membrane of the 1950s and the discovery of the polyelectrolyte complex hydrogel in 1960.

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Ultrafiltration (UF) is a rate-governed separation process in which pressure is the main driving force. The feed solution containing macromolecular solute is introduced into a membrane separator where solvent and certain solutes pass through a semipermeable membrane which is subsequently collected as ultrafiltrate. Both theoretically and practically, UF offers an attractive alternative to a number of conventional separation processes in food processing, chemical processing, and pharmaceutical and medical industries (1, 2). Glimenius (3) presented some observations, viewpoints, and trends of UF for various industries.

An attractive feature of membrane processes is that they are simple in operation and do not require a phase change. One of the problems associated with membrane processes is the phenomenon of concentration polarization due to the resistance offered by the boundary layer. Since a selective membrane rejects dissolved solutes of molecular weight greater than the MWCO, the rejected constituents accumulate in the vicinity of the membrane, giving rise to concentration polarization. This drawback is perhaps the most important reason for the relatively slow acceptance of the ultrafiltration process in industry and the reason that it has not fulfilled its early promise.

Various works have reported on analysis of limiting flux phenomena in ultrafiltration (4–6). Some works were oriented toward the prediction of permeate flux based on some parameters and operating conditions (7, 8). However, very little attention has been paid in analysis to the prediction of rejection during ultrafiltration of macromolecular solutes.

The present work was undertaken in an attempt to develop a mathematical model capable of predicting rejection utilizing the value of three parameters: solvent permeability (based on membrane hydraulic resistance), solute permeability, and reflection coefficient. The main advantage of the developed model is that once these three parameters are known (7, 9), rejection can be predicted at any operating condition determined by bulk concentration, pressure differential, and stirrer speed. No such studies for development of a mathematical model have been made, and therefore this work should help in analyzing mass transfer characteristics during ultrafiltration of these type of solutes under various hydrodynamic conditions. The present work also deals with an attempt to obtain a generalized formulation which takes into account steady-state behavior in continuous stirred ultrafiltration. Further, the model combines the results obtained from irreversible thermodynamics (10) to predict rejection. Poly(ethylene glycol) 6000, a standard macromolecule, was used to compare the results obtained with a stirred batch cell modified to work in a continuous mode (7, 9).

MATHEMATICAL MODEL

Figure 1 shows the concentration polarization phenomena over a membrane. At steady-state there will be no accumulation over a differential element of thickness Δx, and only convective and backdiffusive flux will occur at the two surfaces of the element. A steady-state solute mass balance over the element, lying at distance x from the membrane surface, gives

$$\left[\{Jc|_{x+\Delta x} - Jc|_x\}A_m t + \left\{\frac{dc}{dx}\bigg|_{x+\Delta x} - \frac{dc}{dx}\bigg|_x\right\} D A_m t\right] = 0 \qquad (1)$$

If the diffusivity D and the density of the solution are assumed to be independent of the concentration (c) of the macromolecular solutes, the results obtained for Δx approaching zero are

$$J(dc/dx) + D(d^2c/dx^2) = 0 \qquad (2)$$

Though this equation is derived under the condition of constant density, the dependence of density on concentration will be allowed in future analysis. Now, overall solute mass balance across the volume element (2) gives

$$J = -\frac{D}{c - c_p}\frac{dc}{dx} \qquad (3)$$

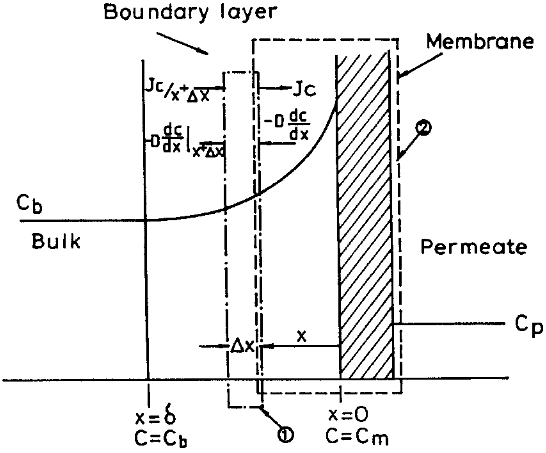

FIG. 1 Mass balance in the film layer.

Substituting Eq. (3) into Eq. (2):

$$\frac{d}{dx}\left(\frac{c}{c - c_p}\frac{dc}{dx}\right) = \frac{d^2c}{dx^2} \tag{4}$$

The above differential equation is solved under the following boundary conditions:

$$\text{b.c.1: At } x = 0, \qquad J = -\frac{D}{c - c_p}\frac{dc}{dx} = L_p(\Delta P - \sigma\Delta\pi)$$

or

$$\left.\frac{dc}{dx}\right|_{x=0} = -\frac{L_p}{D}(\Delta P - \sigma\Delta\pi)(c - c_p) \tag{5}$$

$$\text{b.c.2: At } x = \delta, \qquad c = c_b \tag{6}$$

The first boundary condition is obtained from the fact that flux can be defined as a ratio of driving force to resistance. Solvent permeability ($L_p = 1/\mu_s R_m$) instead of hydraulic resistance is used here in order to be consistent in nomenclature with the work of Nakao and Kimura (10).

Solution of the differential equation with the two boundary conditions gives

$$\ln\frac{c - c_p}{c_b - c_p} = -\frac{L_p}{D}(\Delta P - \sigma\Delta\pi)(x - \delta) \tag{7}$$

At $x = 0$, $c = c_m$, and since film theory suggests that $k = D/\delta$, we get

$$k \ln\frac{c_m - c_p}{c_b - c_p} = L_p(\Delta P - \sigma\Delta\pi) \tag{8}$$

Solute flux can be described from nonequilibrium thermodynamics as

$$J_s = P_m(c_m - c_p) + (1 - \sigma)J\bar{c} \tag{9}$$

where $\bar{c}$ is some sort of average concentration on both sides of the membrane; the logarithmic mean is generally used for this purpose. However, for a membrane with high rejection, the value of $(c_m - c_p)$ is so large that the logarithmic mean does not represent the correct average value. For this case the membrane can be divided into different elements in the direction of its thickness. By using the differential form of Eq. (9), integration (11) gives

$$R = 1 - c_p/c_m = \sigma(1 - F)/(1 - \sigma F) \tag{10}$$

where $F = \exp[-(1 - \sigma)J/P_m]$, with $J = L_p(\Delta P - \sigma\Delta\pi)$. In this equation, R, the real rejection, is a function of membrane surface and permeate concentration, both of which are unknown before an experimental run is performed.

The mass transfer coefficient for a stirred batch cell is given by the following empirical equation (12):

$$k = 0.0443\left(\frac{D}{r}\right)\left(\frac{\nu}{D}\right)^{0.33}\left(\frac{\omega r^2}{\nu}\right)^{0.8}$$

After substituting the experimental value for r, the above equation becomes

$$k = 7.84412 \times 10^{-3} \times D^{0.67} \times \omega^{0.8} \times \left(\frac{\mu}{\rho}\right)^{-0.47} \tag{11}$$

The viscosity and density of PEG-6000 in water solution can be related to a polynomial function of concentration in the following form (8):

$$\begin{aligned}\mu = {} & (0.85 + 0.01446c + 2.734 \times 10^{-4}c^2 - 4.276 \times 10^{-6}c^3 \\ & + 2.84 \times 10^{-8}c^4)/1000\end{aligned} \tag{12}$$

and

$$\rho = (0.9956 + 2.776 \times 10^{-4}c - 9.822 \times 10^{-7}c^2) \times 1000.0 \tag{13}$$

The following correlation was utilized to relate diffusivity to the molecular weight of the polymer solution (13):

$$D = 2.74 \times 10^{-9}M^{-1/3} \tag{14}$$

The osmotic pressure of a solution was determined using Flory's equation (14):

$$\pi = -\frac{RT}{V_1}[\ln \gamma_1 + (1 - 1/x)\gamma_2 + x_1\gamma_2^2] \tag{15}$$

where $x = (V_pM_p)/(V_1M_1)$

γ_1 and γ_2 are concentration-dependent terms and can be expressed as

$$\begin{aligned}\gamma_2 &= c/\rho_p \\ \gamma_1 &= 1 - \gamma_2\end{aligned} \tag{16}$$

where c is the concentration and ρ_p is the density of the polymer in the amorphous state (for PEG, $\rho_p = 1125$ kg/m^3) (15). The value of the parameter x_1 depends upon the type of polymer–solvent interaction ($x_1 = 0.45$ for PEG) (15).

Equations (8) and (10)–(16) all involve concentration-dependent terms. Remembering that $\Delta\pi = \pi_m - \pi_p$, all these equations can be properly substituted to get two highly nonlinear equations with two unknowns (c_m, c_p) in the following forms:

$$f_1(c_m, c_p) = 0 \tag{17}$$

$$f_2(c_m, c_p) = 0 \tag{18}$$

The above two nonlinear equations were solved by the Newton–Raphson method in multidimensional form. An iteration equation can be written in the following form

$$\mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} - \mathbf{J}^{-1}\cdot\mathbf{f}^{(k)} \tag{19}$$

where x is a vector containing the unknown c_m and c_p, i.e., $\mathbf{x} = [x_1, x_2]^T$, $x_1 = c_m$, $x_2 = c_p$, and **J** is the Jacobian matrix. The four elements of the Jacobian matrix, $\partial f_1/\partial c_m$, $\partial f_1/\partial c_p$, $\partial f_2/\partial c_m$, and $\partial f_2/\partial c_p$ can be determined analytically as well as numerically. We have used both methods, but due to the presence of many concentration-dependent terms, the latter method seems to be more suitable from a computational point of view.

For the evaluation of partial derivatives, we have used the following second-order formula:

$$\begin{aligned}\frac{\partial f_i}{\partial x_j} = {} & [f_i(x_1, \ldots, x_j + h, \ldots, x_n) \\ & - f_i(x_1, \ldots, x_j - h, \ldots, x_n)]/(2h)\end{aligned} \tag{20}$$

where $h = 0.0001x_j$ (16).

The above formula is applicable for n equations, and we have used it for a two-dimensional system. Once Eqs. (17) and (18) are solved by the above method, rejection can be calculated by the following formula:

$$R_o = 1 - \frac{c_p}{c_b} \tag{21}$$

and can be compared with the experimentally found rejection value.

RESULTS AND DISCUSSION

For the solution of Eqs. (17) and (18) by the Newton–Raphson method, the initial guess is very important. In fact, $x^{(0)} = [2.0c_b, 0.1c_b]^T$ has been used as our initial guess vector for all runs, and this choice has shown excellent results in terms of rate of convergence. The number of iterations for all the runs never exceeded eight. Therefore this method seems to be quite efficient in predicting c_m and c_p from a computational point of view.

Figure 2 shows the variation of c_m with stirrer speed (ω) at constant bulk concentration (c_b) for two different pressure drops. It is clear from this figure that with an increase in stirrer speed, c_m decreases. The results may be explained on the basis of the fact that a higher stirrer speed increases the turbulence near the membrane surface, which in turn increases backmixing of the deposited solute on the membrane surface into the bulk of the solution. This figure also indicates that the membrane surface concentration increases with an increase in pressure difference for a fixed stirrer speed. As ΔP increases, the permeate flux increases, and this increased flux causes more solutes to be deposited on the membrane. Increased ΔP also causes the deposited solute layer to become compressed, which in turn increases the solute concentration near the membrane surface. This figure also shows that the rate of decrease of c_m with stirrer speed increases with an increase in ΔP.

Figure 3 shows the change in the value of c_m for various values of c_b for a constant stirrer speed. It is evident from the figure that the membrane

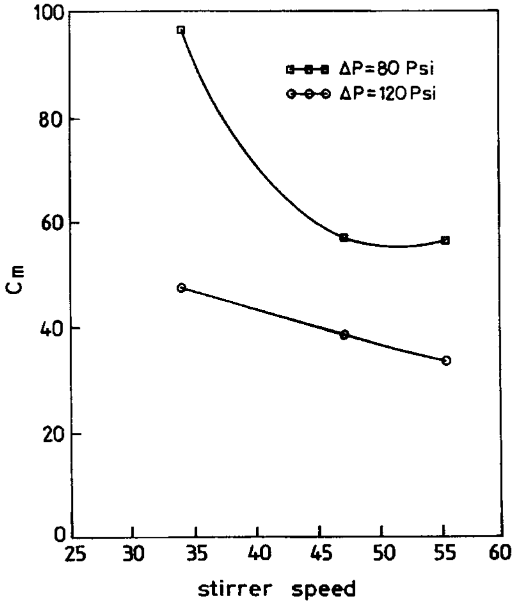

FIG. 2 Variation of membrane surface concentration with stirrer speed at different pressure differentials (c_b = 20 kg/m^3).

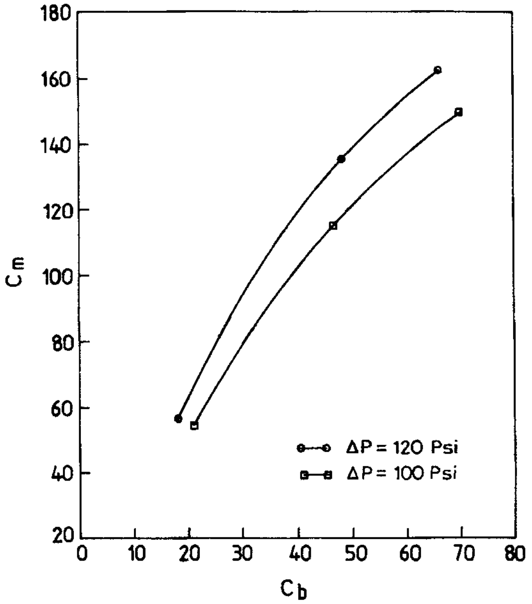

FIG. 3 Membrane surface concentration as a function of bulk concentration at different pressure differentials (stirrer speed = 55.502 rad/s).

surface concentration increases with an increase in bulk concentration, which is obvious. It also shows an increase of c_m with an increase in ΔP, which is in conformity with the results depicted in Fig. 2.

Figure 4 is a plot of calculated rejection vs stirrer speed as well as bulk concentration. This figure shows that rejection increases with an increase in stirrer speed. In fact, as the stirrer speed increases, the more deposited solutes are removed from the membrane surface, and therefore c_m decreases. Furthermore, at a low stirrer speed the high c_m value causes a high concentration gradient to prevail across the membrane, giving a rise to the increase in permeate concentration, which effectively reduces rejection. In fact, this observation may be more pronounced with polymer molecules due to their structures. In this study, PEG-6000 has been used, and therefore the entangled PEG molecule at high c_m may become oriented in the pore direction, and hence more molecules may pass through the membrane. This may also be one reason for the low rejection at low stirrer speed.

Figure 4 also shows the variation of calculated rejection with bulk concentration. As the bulk concentration increases, the membrane surface

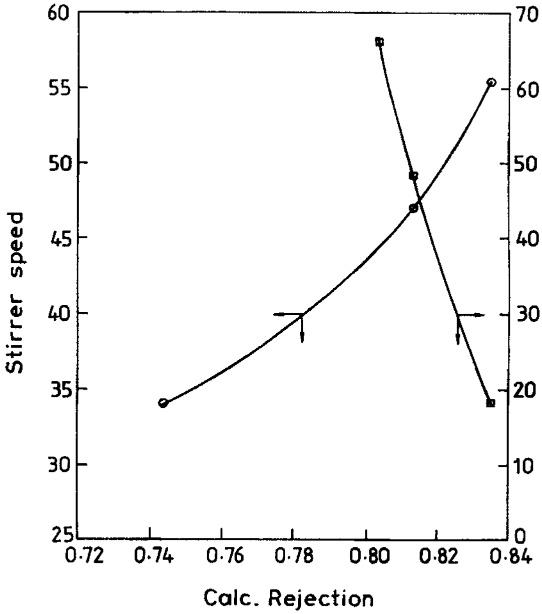

FIG. 4 Calculated rejection as a function of stirrer speed and bulk concentration.

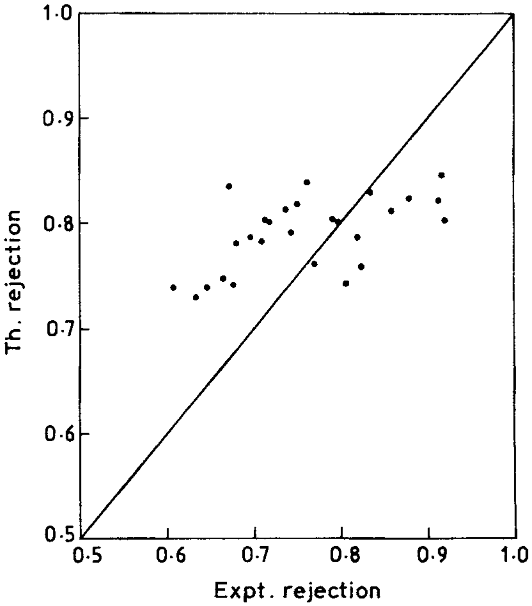

FIG. 5 Comparison of experimental and theoretical rejection calculated from this model.

concentration increases, which may cause the permeate concentration to increase, which ultimately decreases rejection because of the reasons already mentioned. In fact, this observation also supports the previous findings.

Figure 5 shows the predictions of the present model as well as the experimental results of Bhattacharjee and Bhattacharya (7, 9) for ultrafiltration of PEG-6000 in a stirred cell. The present model is in good agreement with the experimental results of Bhattacharjee and Bhattacharya. The deviation shows an equal trend on both side of the zero value, as shown in Fig. 5. In fact, the calculated rejection shows agreement with the experimental value within a ± 10% deviation for most of the experimental run.

NOMENCLATURE

A_m	membrane surface area (m^2)
c_b	bulk concentration (kg/m^3)
c_m	membrane surface concentration (kg/m^3)
c_p	permeate concentration (kg/m^3)
D	diffusivity (m^2/s)
F	variable defined in Eq. (10) (dimensionless)
f_1 or f_2	defining functions in Eqs. (17) and (18)
$\mathbf{f}$	function vector
h	interval width in Eq. (20)
J	permeate volumetric flux ($m^3 m^2 \cdot s$)
$\mathbf{J}$	Jacobian matrix
J_s	solute flux ($kg/m^2 \cdot s$)
k	mass transfer coefficient $= D/\delta$ (m/s)
L_p	solvent permeability $= 1/\mu_s R_m$ ($m^2 \cdot s/kg$)
MWCO	molecular weight cut off
M	molecular weight (kg/kmol)
P	pressure (N/m^2)
P_m	solute permeability (m/s)
PEG	polyethylene glycol
r	radius of membrane (m)
R	gas constant; also real rejection
R_o	observed rejection, defined by Eq. (21)
R_m	membrane hydraulytic resistance (m^{-1})
t	time (second)
UF	ultrafiltration
V_1, V_P	specific volume of solvent and polymer (m^3/kg)

x	distance in the film layer from membrane (m); also a variable defined by Eq. (16)
x_1	value dependent upon polymer–solvent interaction
$\mathbf{x}$	vector, $x = [x_1, x_2]^T$ where $x_1 = c_m$, $x_2 = c_p$

Greek Letters

γ_1, γ_2	parameter defined by Eq. (16)
μ	viscosity (kg/ms)
ω	angular velocity (rad/s)
π	osmotic pressure (N/m^2)
ρ	density (kg/m^3)
ν	kinematic viscosity, μ/ρ (m^2/s)
σ	reflection coefficient
δ	film thickness

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Received by editor March 24, 1995