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The Mechanism of Partial Rejection by Ultrafiltration Membranes

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Abstract

For molecules only slightly smaller than the pores of a membrane, the fraction rejected depends on product flow rate, molecular shape and diffusivity, and membrane structure. A significant factor for dilute solutions is the reduced flow of solution in pores containing a solute molecule compared to the flow of solvent in adjacent empty pores.

INTRODUCTION

Ultrafiltration and reverse osmosis are separation processes that rely on a pressure difference across a membrane for transport of water or other solvent. Typical ultrafiltration membranes have a connected network of pores with a mean diameter between 20 and 100 Å, which is large enough for laminar flow of water but small enough to exclude large solute molecules or colloidal particles. Reverse osmosis membranes are designed to reject ionized salts and small molecules, and if they can be considered to have pores, the pores must be less than 20 Å in diameter. For such tight membranes it is difficult to distinguish between transport through definite pores and a solution-diffusion mechanism of transport. This paper primarily discusses ultrafiltration membranes, but the theory may be applicable to the coarser types of reverse osmosis membranes.

The name ultrafiltration comes from the concept that the membrane acts as a sieve, screening out molecules larger than the pore size. Small solute molecules and solvent pass through the pores, while large molecules are rejected at the membrane surface and form a more concentrated solution on the upstream side. A sharp molecular weight cutoff is not expected because most membranes have a distribution of pore sizes. Intermediate size molecules will pass through some of the pores but will not be able to enter the finest pores, and this leads to partial rejection or a lower concentration in the permeate solution than in the feed. However, for commercial membranes, there is a wide range of molecular weights (50–100-fold) between solutes having almost zero rejection and those with almost complete rejection (*1*), suggesting either a very wide range of pore sizes or an alternate mechanism of partial rejection for intermediate size molecules.

PARTITION THEORY

A proposed modification of the sieving theory was based on a sieving factor, defined as the ratio of product concentration to concentration at the wall (*2*). While this partly accounts for the effect of polarization on rejection, it does not allow for the concentration gradients within the membrane. An equilibrium distribution should be assumed at both surfaces of the membrane, as in Merten's treatment (*3*). In the following equations, the internal concentration C_{pore} is based on the volume of pore fluid, whereas Merten's C_m is based on the total membrane volume:

$$C_{\text{pore}} = KC_w \tag{1}$$

The partition factor K is less than 1.0 because some of the pore volume is accessible to solvent but not to the larger solute molecules. Theories and some data for K are discussed later. If K is the same at both surfaces of a uniform membrane, the gradients during steady-state ultrafiltration would be as shown in Fig. 1a. For an asymmetric membrane with a sharply-defined skin and a large pore substructure, the gradients of Fig. 1a would apply to the skin layer, and there would be no gradient in the substructure. If the transition from the fine pores in the skin to the large pores in the supporting layer is not abrupt, there would be a gradual increase in pore concentration in this region, as shown in Fig. 1b. To avoid the complications of dealing with a gradual change in membrane characteristics, the gradients are assumed to be as shown in Fig. 1a.

The flux of solute within the membrane depends on the flow of solution and the diffusion of solute relative to the center of mass. Merten (*3*) showed that for dilute solutions and moderately permeable membranes

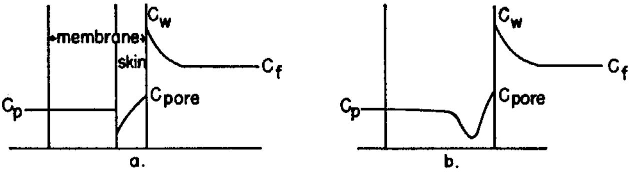

FIG. 1. Concentration gradients in ultrafiltration membranes. (a) Idealized asymmetric membrane. (b) Membrane with gradual transition to large pores.

the following simplified equation could be used:

$$F_2 = uC_{\text{pore}} - D_e\left(\frac{dC_{\text{pore}}}{dy}\right) \tag{2}$$

Integration of Eq. (2) and assumption of the same partition factor at both boundaries leads to

$$\frac{C_p}{C_w} = \frac{K \exp(uL/D_e)}{K - 1 + \exp(uL/D_e)} \tag{3}$$

where L = membrane (or skin) thickness and, $D_e = D_{\text{pore}}\varepsilon/\tau$.

To determine the solute rejection based on the feed side concentration, mass transfer in the external boundary layer must be considered. For steady-state diffusion of rejected solute back to the feed solution, the equation of de Filippi and Goldsmith (*4*) would apply:

$$u = k \ln\left(\frac{C_w - C_p}{C_f - C_p}\right) \tag{4}$$

The rejection could then be predicted by solving Eq. (3) and (4) for a given set of membrane parameters and external transfer coefficient k. As indicated by Eq. (3), the rejection approaches zero at low product flux because molecular diffusion in the pores tends to equalize the concentration on both sides of the membrane. If we consider only the membrane selectivity and base the rejection on concentration at the wall, the rejection would approach a limit of $1 - K$ at high product rates. However, because concentration polarization becomes more severe at high rates, the actual rejection eventually decreases with increasing flow, giving a maximum in the graph of rejection versus product rate. Most ultrafiltration data show a decrease in rejection with increasing flow because the data are taken at high fluxes where the effect of concentration polarization dominates.

HINDERED FLOW THEORY

A weakness of the previous theory is that the solution in the pores is treated as a continuum, with concentration depending only on distance from the membrane surface. Since the pores are only slightly larger than the molecules that are partially rejected, and since frequent pore intersections make the length of a pore quite short, the concentration of solute will vary from pore to pore at the same depth. If the average concentration is low, say 1.0%, most pores will have no solute molecules, some will have one, and very few pores will have two. A cross section of a membrane with random pores is shown in Fig. 2.

Some partition of solute between the external solution and the pore fluid is assumed, as in the previous theory, and there is a diffusion flux because of a gross concentration gradient. However, the first term in Eq. (2) must be modified because more solvent will flow through an open pore than through an adjacent pore which has a large molecule occupying much of the volume. Flow through open pores does not contribute to the convective flux of solute and the flux of solute is less than uC_{pore}, even if each solute molecule moves at the average velocity of the fluid which surrounds it. To develop this concept further, the hindrance to flow is considered for randomly oriented polymer molecules and for spherical molecules such as globular proteins or viruses.

POLYMER MOLECULES

A polymer molecule in a pore creates a local region of high concentration and high viscosity. The flow of solution is assumed to vary inversely with the effective average viscosity in the pore. Consider the dilute solution case where there is only one polymer molecule per pore in α fraction of the pores and none in the remaining fraction. The total solution flow is expressed in terms of the flow of solvent with no solute present, u^*, and the ratio of solvent viscosity to viscosity in an occupied pore:

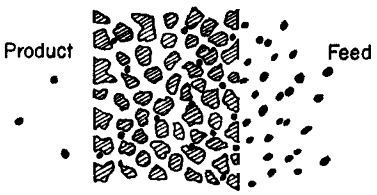

FIG. 2. Cross section of ultrafiltration membrane.

$$u = u^*(1 - \alpha) + u^*\alpha\left(\frac{\mu_0}{\mu}\right) \tag{5}$$

The solute is carried only in occupied pores, which have local concentration C_{pore}/α:

$$\text{solute carried} = \left(u^*\alpha\frac{\mu_0}{\mu}\right)\left(\frac{C_{\text{pore}}}{\alpha}\right) \tag{6}$$

In terms of the measured product flow, the convective solute flux is:

$$\text{solute carried} = \frac{u}{\left(1 - \alpha + \alpha\frac{\mu_0}{\mu}\right)}\left(\frac{\mu_0}{\mu}\right)C_{\text{pore}} \tag{7}$$

For dilute solutions, α is nearly zero and the denominator term in Eq. (7) can be dropped. The equation for total solute transport then becomes:

$$F_2 = u\left(\frac{\mu_0}{\mu}\right)C_{\text{pore}} - D_e\left(\frac{dC_{\text{pore}}}{dy}\right) \tag{8}$$

This is the same as Eq. (2) except for the term (μ_0/μ), and the product concentration is:

$$\frac{C_p}{C_w} = \frac{K\left(\frac{\mu_0}{\mu}\right)\exp\phi}{K\left(\frac{\mu_0}{\mu}\right) - 1 + \exp\phi} \tag{9}$$

where $\phi = uL/D_e(\mu_0/\mu)$. The rejection based on the wall concentration is plotted in Fig. 3.

A significant feature of this model is that the maximum rejection (based on C_w) is $1 - K(\mu_0/\mu)$ rather than $1 - K$. For example, a distribution coefficient of 0.2 and a viscosity ratio of 0.25 means a potential rejection of 95%. Even if the distribution coefficient is 1 or greater than 1, as has been reported for a few systems (*5*, *6*), high rejection is possible if solute molecules appreciably hinder the flow of solution through occupied pores.

A sample calculation based on the hindered flow theory was made for polyethylene oxide in water in membranes with uniform cylindrical pores. The average pore length between intersections was assumed to be equal to the pore diameter, so that each pore had a volume $\pi d^3/4$. The weight percent polymer in an occupied pore was calculated for one molecule per pore, and the viscosity was assumed the same as for a bulk solution of that concentration. The viscosity ratio and the maximum rejection are

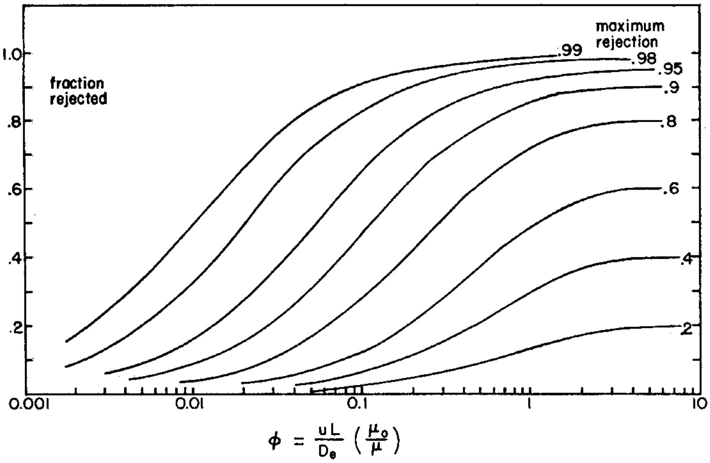

FIG. 3. Rejection of solutes by ultrafiltration membranes.

shown in Fig. 4 as a function of molecular weight for 25 Å radius pores. The radius of the polymer molecules was calculated from $r^2 = Nb/6$ (*7*), where N is the number of segments and b the segment length. The partition coefficient K was taken from Casassa's plot (*7*) for polystyrene in porous glass, which approximately fits the equation $K = 1 - r/R$. The maximum rejection varies from 40 to 99% over a 6-fold range of molecular weights, showing that a sharp cutoff cannot be expected even with a uniform pore size.

To show the effects of molecular diffusion within the membrane and concentration polarization, Eq. (9) was applied with the following parameters. The membrane was assumed to have a 1 or a 0.2-μ skin with 40% voids, a tortuosity of 2, and a pore radius of 25 Å. (The calculated water flux at 10 psi is 23 gal/day, ft^2 for a 1-μ skin.) The bulk diffusivity for 5000 molecular weight polyethylene oxide is 1.2×10^{-6} cm^2/sec, and this was reduced by the empirical factor $(1 - r/R)^3$ to get a pore diffusivity. Beck and Shultz (*8*) found a hindered diffusion factor of about $(1 - r/R)^4$, but this included a distribution coefficient which was assumed to be $(1 - r/R)$. The estimate of D_{pore} is very uncertain because there are no data for ($r/R > 0.5$. The mass transfer coefficient was taken as 6×10^{-4} cm/sec, based on Goldsmith's data for stirred-cell ultrafiltration of polymer solutions (*2*).

As shown in Fig. 5, the predicted rejection goes through a maximum at a flux of 2–4 $\times 10^{-4}$ cm/sec and then drops sharply because of polariza-

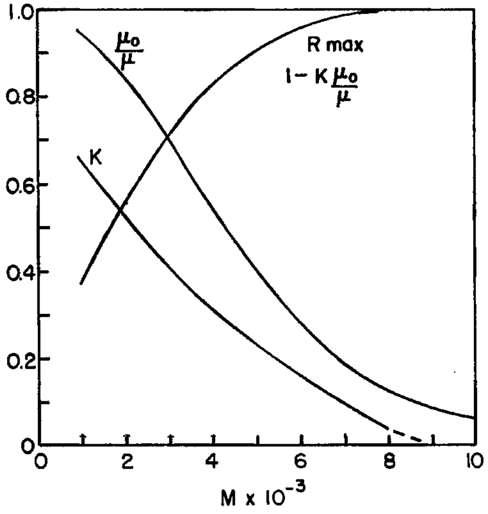

FIG. 4. Maximum rejection for polyethylene oxide by membrane with 25 Å pores.

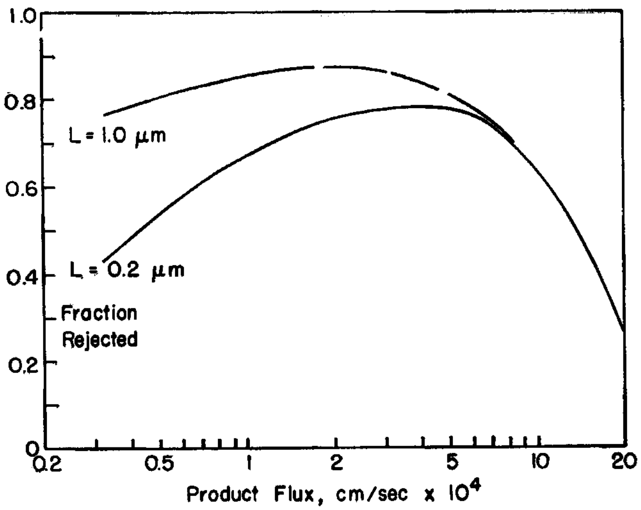

FIG. 5. Predicted rejection of polyethylene oxide, $M = 5000$, for $R = 25$ Å, $k = 6 \times 10^4$ cm/sec.

tion. With a 1-μ skin, the maximum rejection is 87% compared with a possible value of 91%. If the membrane skin is 0.2 μ, there is a greater effect of molecular diffusion, particularly at low product rates.

SPHERICAL MOLECULES

The viscous flow of liquid through a cylindrical tube containing rigid spheres was discussed by Wang and Skalak (*9*). They considered a chain of spheres equally spaced along the axis of a long tube, and their calculations for a center-to-center spacing equal to the tube diameter are used here to estimate the effect of a single spherical molecule in a short pore segment. The main effect of a molecule almost as large as the pore is to lower the flow for a given pressure gradient and, if only a fraction of the pores have any solute molecules, the velocity in the occupied pores will be less than in the empty pores. The ratio of these velocities is shown as a function of the radius ratio in Fig. 6. This ratio v/v^* would replace μ_0/μ in Eq. (5) to (9), and Fig. 3 would then apply to dilute solutions of either rigid molecules or polymer chains. However, note that the hindrance to flow caused by a rigid molecule is expected to be less than that caused by a high molecular weight polymer. For a sphere, v/v^* is 0.45 at $r/R = 0.9$, whereas the viscosity ratio might be 0.05 to 0.10 for a polymer chain of the same radius.

A secondary effect of a rigid sphere in a pore is that the sphere tends to be carried along at a velocity greater than the average fluid velocity. Even though a molecule or particle takes random positions because of Brownian motion, it is confined to a region between the center and a distance r from the wall, where the average velocity exceeds that for the entire pore. For Wang and Skalak's case, where the sphere was on the centerline, the ratio of sphere velocity to average fluid velocity approached 2.0 for small spheres and was 1.14 for $r/R = 0.9$. Since their ratios are

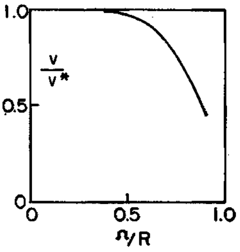

FIG. 6. Hindrance to flow for a sphere in a circular pore.

too high for molecules that have random radial positions, yet are not far from 1.0 for the most interesting case of a molecule nearly filling the pore, the effect is neglected in this analysis.

DISCUSSION

The main feature of the hindered flow theory is that the flow of solution is assumed to be smaller in pores containing a single solute molecule than in empty pores. This effect does not change the general shape of the rejection curve but does make the maximum possible rejection greater than $1 - K$. Other models which give rejections greater than $1 - K$ have been presented, but they are based on different premises. In Merten's (*3*) approach, which follows earlier work by Spiegler and Kedem and Katchalsky, the frictional interaction between solute and membrane is assumed proportional to solute velocity, and the convective flux and the diffusion flux in Eq. (2) are both reduced by a factor $1/b$, where $b = 1 + f^{23}/f^{21}$. However, it seems possible to have no frictional interaction between a solute and the pore wall and yet have a diffusivity much less than the bulk value because the wall restricts the Brownian motion of the solute. The pore diffusivity is about 0.1 the bulk value for a molecule half the size of the pore (*8*), which corresponds to $b = 10$. According to the frictional interaction theory, such a molecule would be carried along at only 0.1 the average pore velocity, which seems unlikely. A randomly arranged polymer chain would have portions of the molecule throughout the pore cross-section, and drag on the chain segments would tend to move the molecule with little or no slip. If the molecule were a rigid sphere, it might even move slightly more rapidly than the average fluid.

The theory presented here does not exclude the possibility of an additional factor for solute retardation caused by adsorption on the wall or entanglement of a polymer chain in two pores. These interaction effects would decrease the average convective solute velocity, though adsorption would also increase the total solute concentration. These effects would also cause a further decrease in the effective diffusivity, but the overall factor for decrease in diffusivity and the total reduction in convective flux because of hindered solution flow and slip between solute and solvent might be quite different and should be considered separately.

It is difficult to check the proposed theory using published results because there is very little data on partition factors or diffusion coefficients for molecules in small liquid-filled pores. For the example presented here, K was assumed to be $(1 - r/R)$ based on limited data for polystyrene in porous glass. Casassa (*7*) presents a thermodynamic derivation for random polymer chains in different types of pores, and his predictions for a flat plate model are in fair agreement with the data, though K's predicted for circular pores are much too low. The pores in a membrane are probably more like void spaces in a packed bed than either circular pores or the spaces between flat plates, and agreement with a theory based on any simple shape might be a coincidence. The partition coefficient may be influenced by polymer–membrane interactions. Jellinek and Bloom (*6*) reported that K ranged from 1.7 to 4.3 for polyvinylpyrrolidone in cellulose ester membranes, indicating adsorption of polymer. However, the effective diffusivities were not very much below the bulk values, showing that the polymer was free to migrate in the membrane.

For spherical molecules in small cylindrical pores, many workers have used the Renkin equation, with $K = (1 - r/R)^2$. Giddings and coworkers (*10*) have extended the Renkin approach and presented theoretical distribution coefficients for spheres and other rigid molecules in various types of pores. However, the derivations assume no molecule–wall interaction and may be greatly in error for r/R close to 1.0. Imagine a pure solvent with molecules 9 Å in diameter entering a solid with 10 Å pores. Since the centers of the molecules are restricted to the central 1% of the pore cross-section, the Renkin equation predicts that only 1% of the pore volume is occupied, which seems much too low. Haller (*5*) found $K \cong 1$ for a spherical virus in porous glass with $r/R = 0.4$. Perhaps K values of less than 1 come primarily from a pore size distribution which makes some portion of the pore volume truly inaccessible to the solute.

It would be helpful to have more data on the partition factor and diffusion in small pores for both compact molecules and polymers, but it would be very difficult to get such data using typical ultrafiltration membranes because the skin layer is such a small fraction of the membrane thickness. Tests on uniform membranes or porous particles will have to be combined with pore size data to predict K for ultrafiltration membranes.

For a thorough treatment of ultrafiltration, the effects of a pore size distribution and a molecular weight distribution for the solute would also have to be considered. The hindered flow theory predicts that a solute molecule will spend proportionately more time in small pores than in large pores as it travels through the membrane, which tends to decrease the effective average pore size. If there are several solutes, the rejection for each based on C_w is calculated separately as long as the concentrations in the membrane are low enough so that few pores have more than one solute molecule. The complication arises from calculating the wall concentration for each solute, since all partially rejected solutes contribute to an increase in the osmotic pressure, which affects the product flow, and to an increase in the viscosity of the solution near the wall, which affects the diffusion flux in the boundary layer.

SYMBOLS

C_f	solute concentration on the feed side of the membrane
C_m	solute concentration, mass per unit volume of membrane
C_{pore}	solute concentration, mass per unit volume of pore
C_p	solute concentration in the product
C_w	solute concentration at the wall or membrane-solution interface
d	pore diameter
D_e	effective diffusivity, $D_{\text{pore}}\varepsilon/\tau$
f_{21}	friction coefficient, solute-solvent
f_{23}	friction coefficient, solute-membrane
F_2	solute flux, mass/total area, time
k	mass transfer coefficient for external boundary layer, length/time
K	partition factor, C_{pore}/C_w
L	membrane (or skin) thickness
r	radius of solute molecule
R	pore radius
u	product flux, volume/total area, time
u^*	flux with no solute in the feed
v	particle velocity in a pore
v^*	velocity of solvent in an empty pore
y	distance normal to the surface
α	fraction of pores containing a solute molecule
ε	void fraction
τ	tortuosity
μ	viscosity of solution in a pore
μ_0	viscosity of solvent
ϕ	defined by Eq. (9)

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