Ultrafiltration of Macromolecular Solutions with High-Flux Membranes

R. W. BAKER, Polytechnic Institute of Brooklyn, Brooklyn, New York 11201 and H. STRATHMANN, Technische Hochschule, Institut für Physik und Chemie, Aachen, Germany

Synopsis

Batch and flow recirculation cells were used to study the properties of high-flux ultrafiltration membranes with different macromolecular solutions. At low pressures, solutions of completely retained macromolecular solutes have a flux which is approximately the same as the flux of pure solvent. At higher pressures, the solution flux levels off. The flux, at the leveling-off period, is approximately inversely proportional to the solution concentration. In this plateau region the flux increases with temperature and agitation of the solution but decreases with time. These results are explained by the formation of a gel layer on the membrane surface during the filtration of macromolecular solutions. In ultrafiltration, in contrast to dialysis and GPC, a linear polymer penetrates the selective barrier more readily than does a globular protein of the same molecular weight. The difference may arise from the liquid shear stresses within the barrier medium due to the movement of fluid relative to the pore walls, which is large only in ultrafiltration. Also, retention of polymers was found to decrease with pressure and to increase with agitation of the solution.

INTRODUCTION

Separation and concentration of macromolecular solutions and colloidal suspensions by ultrafiltration under pressure can be achieved by a permselective membrane which allows passage of solvent and small solutes but retains larger units. The two most important properties of such membranes are the product flux rate and the retention of the solute. The flux of macromolecular solutions, with membranes which have high fluxes for pure water, will be shown to depend mainly on the type of solute, the concentration of the solution, the degree of agitation of the solution, and on the temperature. The retention will be shown to depend mainly on the nature of the membrane.

In ultrafiltration of macromolecular solutions, the product flux is usually much less than the pure water flux. In the ultrafiltration of microsolutes, a similar reduction in flux is found due to the accumulation of retained solutes at the membrane surface. This concentration polarization reduces the solvent flux by increasing the osmotic pressure which has to be overcome

* Present address: Technische Hochschule, Institut für Physik und Chemie, Aachen, Germany.

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by the applied pressure. With macromolecular solutions, the osmotic pressure is too small to explain the reduction in flux, nor can internal membrane plugging be the cause since mild washing of the membrane results in the rapid return of the flux of pure water to its original value. Rather, it appears that a layer of concentrated colloid or gel is deposited on the ultrafiltration membrane. This layer acts in series with the underlying membrane to form a barrier to the flow of solvent and low molecular weight solutes.^{1,2} Solutions of completely retained macromolecular solutes were used to study the consequences of gel layer formation on the trans-membrane flux. This avoided the complications of partial retention.

Solute transport through ultrafiltration membranes has been examined with partially retained solutes. We believe that two mechanisms affect the retention during ultrafiltration. These are the alignment or deformation of macromolecules inside the membrane pores as a result of high fluid shear rates and the effects of excessive concentration polarization. The probability of chain alignment inside the membrane may be derived from a simple calculation. A typical trans-membrane flux of a polymer solution is ca. 0.2 cm/min which corresponds to a mean velocity inside the membrane pores (skin porosity 0.5) of 0.4 cm/min. It might be thought that the effect of such a low velocity should be slight. However, the pores in our membranes are exceedingly small, ca. 20–100 Å radius. The velocity gradient is therefore correspondingly large and in the region of $2-5 \times 10^4$ sec. This shear rate is sufficient to alter the configuration of many macromolecules. The membrane flux therefore has a considerable effect on the passage of solute. Concentration polarization, by increasing the concentration of solute at the membrane surface, also decreases the retention of solute because the trans-membrane solute flux is directly proportional to the concentration at the membrane surface.

EXPERIMENTAL

Materials

For the retention studies, 1% solutions of dextran (supplied by Pharmacia, N. J., under the names Dextran 80 ($M_w \sim 80,000$), Dextran 40 ($M_w \sim 40,000$), etc.) and polyethylene glycols (trade name Carbowax, supplied by Union Carbide) and 0.25% solutions of various proteins were used. The concentrations of most materials were measured with a differential refractometer, except for two of the protein solutions, insulin and bacitracin, which were more dilute and which were measured spectrophotometrically.

The Membranes Used

Diaflo membranes were used throughout this work (supplied by Amicon Corporation, Lexington, Massachusetts). The two letters in the membrane code name give the material of the membrane. The two figures indicate the approximate pore size on an arbitrary scale. Thus, membrane UM-10 retains smaller molecules than does PM-20. The UM membranes are made of ioplex, a polyelectrolyte complex. The other membranes are made of nonionic conventional vinyl polymers. The XM, PM, and UM series are obtainable commercially; the LM and VM membranes were supplied on an experimental basis.

The Ultrafiltration Systems

The Batch Cell

The batch cell apparatus used in this work has been described previously.³ It consisted of an Amicon Model 401 cell with a volume of \sim 400 ml and an effective membrane area of 32 cm². The cell contained an internal magnetic stirrer.

The Recirculation Cells

A recirculation system with rectangular channel ultrafiltration cells was used to examine concentration polarization at controlled feed fluid velocities. A diagram of the system is shown in Figure 1. Several cells,



Fig. 1. Schematic diagram of flow through recirculation apparatus.

with various channel heights, were used. A centrifugal pump capable of delivering up to 3 gallons per min at a pressure drop of 40 psi recirculated fluid through the system. An external nitrogen cylinder attached to the feed reservoir could effect changes in the average ultrafiltration pressure.

Procedures

The rejection coefficient R is defined⁴ as follows:

$$R = 100 \left(1 - \frac{C_f}{C_b}\right)\%$$
(1)

where C_f is the concentration of solute in the filtate and C_b is the concentration in the bulk. The rejection coefficient was measured with batch cells by two methods.

If the solute was inexpensive, a 400-ml cell was filled with solution, the pressure was applied, and a small volume of filtrate was collected. The concentration C_b was little changed by the removal of a small volume of filtrate and the rejection coefficient was calculated directly from eq. (1). The membrane was washed with water and a fresh solution was added. The experiment could then be repeated at a different pressure.

For the albumin- γ -globulin mixtures it was impracticable to use large volumes of solution and so the rejection coefficient was determined by a diafiltration technique.⁵ A 60-ml batch cell containing the test solution was connected to a reservoir containing pure solvent. The pressure was then applied to the reservoir. The filtrate was continuously replaced by solvent from the reservoir, keeping the volume of the test solution constant. The solute concentration in the cell fell as it was gradually eluted into the filtrate. The filtrate concentration as a function of the total filtrate volume was then given by

$$-\ln C_{f_{(t)}} = \text{const} + [1 - (R/100)] \frac{V_{(t)}}{V_0}$$
(2)

where $V_{(t)}$ was the volume filtered at time t when the concentration in freshly eluted filtrate was $C_{I(t)}$ and V_0 was the cell volume. A plot of $-\ln C_{I(t)}$ against $V_{(t)}/V_0$ gave a slope of [1 - (R/100)].

RESULTS AND DISCUSSION

The Trans-Membrane Flux

The Gel Layer Model

During ultrafiltration there is an increase in the solute concentration at the membrane surface over the bulk solution concentration. This is called concentration polarization.^{6,7} Both the solvent and the solute are carried to the membrane surface by convection with the product flux. Since only the solvent and small solutes can permeate the membrane, solutes above a certain molecular size accumulate at the membrane surface. This accumulation markedly affects the membrane properties. The rate at which the retained solutes are transported back into the solution governs the extent to which accumulation occurs.

The fluxes of rejected solute to and from the membrane surface reach a steady state when no further accumulation of solute takes place in the membrane boundary layer. This may be expressed by

$$\xrightarrow{\text{to}}_{J_s} + \xleftarrow{\text{from}}_{J_s} = 0 \tag{3}$$

where \underbrace{from}_{J_s} is the mass flux of a solute from the membrane surface in grams/(min cm²) and \underbrace{to}_{J_s} is the mass flux of solute to the membrane surface in grams/(min cm²). The volume flux through the membrane multiplied by the concentration of the solute at this point gives the mass flux. Hence

$$J_w C + \stackrel{\text{from}}{\longleftarrow} J_i = 0 \tag{4}$$

where J_w is the volume flux in cm³/(min cm²).

In eq. (4), $\frac{from}{Js}$ is rate determining at high fluxes or high solute concentrations. In this case the flux depends on the rate of dissipation of solute back into the bulk rather than on the permeability of the membrane. The simplest treatment of the solute dissipation process is to assume that it is normal molecular diffusion. Equation (4) may then be written as

$$D\frac{dC}{d_x} = J_w \cdot C \tag{5}$$

where D is the solute diffusion coefficient and dC/dx is the concentration in gradient. The theories of concentration polarization used in the studies of reverse osmosis of saline water are then applicable. This problem has been studied by several authors⁸⁻¹⁰ who postulate a steady state similar to eq. (5). Replacing the membrane-solution interface by the gel layersolution interface and assuming that this interfacial concentration, C_{g} , cannot exceed the gel concentration for the system being ultrafiltered, we may write for the case of a turbulent flow-through cell¹¹

$$\frac{C_{g}}{C_{b}} = \exp\left\{\frac{0.58 \cdot J_{w} \cdot \eta^{0.42} \cdot h^{0.25}}{D^{0.67} \cdot u^{0.75}}\right\}$$
(6)

where η is the kinematic viscosity, *h* is the cell half channel height, and *u* is the bulk fluid velocity. A similar equation exists for the stirred batch cell.¹²

The analysis upon which eq. (6) is based limits its usefulness to ultrafiltration membranes. Fully developed turbulent flow in the ultrafiltration cell is assumed. This is rarely the case.¹² Furthermore, the solute diffusion coefficient is assumed to be a constant. With macromolecules this is incorrect and the diffusion coefficient is a function of concentration and shear rate in the bulk liquid. If a value of D obtained from sedimentation experiments is used and eq. (6) is assumed to be valid, the calculated concentration polarization is unrealistically large. In part this may be due to



Fig. 2. Product flux of a completely retained albumin solution at two different pressures. Data obtained with a batch cell and UM-10 membranes. Above 1% protein concentration, flux obtained is much less than pure water flux and is almost the same at 50 psi as at 100 psi.



Fig. 3. Flux pressure relationship for serum proteins. The proteins are completely retained by these membranes. At low pressures the flux is a large fraction of the water flux and increases with pressure.

the approximations in the use of eq. (6). However, it is possible that solute is also being removed from the membrane as nondisassociated gel particles by the shear gradient at the membrane wall.

The Effects of Pressure and Concentration

The gel layer model outlined above offers an explanation for the results in Figures 2 and 3. At low flux rates, \xrightarrow{to}_{J_s} is easily balanced by \xleftarrow{from}_{J_s} , and in this low pressure region the flux increases with increasing pressure.

As the flux is increased, a pressure is reached at which no further increase in \xrightarrow{to}_{J_s} can be balanced by the back transport away from the membrane surface. At this point further increases in pressure result only in a thicker or denser gel layer and the flux remains constant. It follows from eq. (2) that the plateauing of the flux occurs at a lower pressure on increasing the feed concentration. The flux in the plateau region is approximately inversely related to the concentration of the solution, in accord with eq. (4).

The Effect of Agitation

Equation (4) predicts that when a gel layer is formed an increase in the product flux can be obtained by increasing the dissipation of solute into the bulk solution but not by increasing the pure water permeability of the membrane. Increased agitation of the feed solution causes a gradual dissolution of the gel layer with a subsequent increase in permeability of the system. The trans-membrane flux, J_w , then rises to a value at which the



Fig. 4. Flux/time plot of a casein solution in a flow recirculation system. This experiment shows both the effect of solution feed velocity and the reversible decay of flux with time.

two solute transport rates are again balanced. This agrees with the experimental results in Figure 4. In our experiments the flux of macromolecular solutions in the gel-controlled region did not depend on the initial pure water permeability of the membrane.



Fig. 5. Typical plot of ultrafiltration flux against time, carried out in a flow recirculation system. The concentration of the retained case in is kept constant by replacing the filtrate volume with water from the back-up reservoir.



Fig. 6. Graph showing the flux over a long period of time. Note the sharp increase in flux on increasing the temperature after 55 hr. Results were obtained with a completely retained 1% case in solution in a flow recirculation system.

The Effect of Temperature and Time

A gel which controls the trans-membrane flux offers an attractive explanation for the drop in flux with time shown in Figure 5. A gel might gradually harden as ultrafiltration continues to result in a drop in flux. The slight rise in flux in Figure 4 when an experiment is stopped for 40 min is possibly due to the reversible nature of this gel hardening. The increased flux with increased temperature shown in Figure 6 could also be explained by the greater fluidity of gels at elevated temperatures.

The Membrane Structures

The membranes are approximately $100 \ \mu$ thick, with a dull and a shiny side. A cross section viewed under the optical microscope has the appearance of a sponge, with a gradual decrease in pore size from the dull to the shiny side. The electron microscope shows this gradation in pore size in more detail. Figure 7, an electron micrograph of a membrane cross section, shows a 1μ to 2μ -thick retentive surface layer.

The extremely small pore size and high anisotropy of the membrane preclude the use of conventional pore size characterization techniques. Thus the intrusion pressure on a dried membrane is in excess of 100 psi, which only shows the pore radii to be smaller than 2000 Å. Higher pressures cause collapse of the membrane.



Fig. 7. Electron micrograph of cross section of a typical membrane.

Ferry¹³ was the first to use molecular retention measurements to obtain pore radii. He assumed the pores to be equal circular capillaries whose radius, r, is large compared to the radius of the solvent molecules. The total area of the capillary is therefore available for transport of solvent.



Fig. 8. Experimental retention profiles using globular proteins and calculated retention profiles from eq. (10).

A solute molecule whose radius, a, is an appreciable fraction of the pore radius cannot approach nearer than one molecular radius to the pore wall. The area, A, of the pore available for transport of solute is then given by

$$\frac{A}{A_0} = \frac{(r-a)^2}{r^2}$$
(7)

where A_0 is the area of the pore available for solvent molecules. Equation (7) has to be modified to account for the parabolic velocity of the fluid in the pore.¹³ The effective fractional pore area available for solute in this case is

$$\left(\frac{A}{A_0}\right)' = 2\left(1 - \frac{a}{r}\right)^2 - \left(1 - \frac{a}{r}\right)^4 \tag{8}$$

where the ratio $(A/A_0)'$ is equal to the ratio of the concentration of solute in the filtrate to the concentration in the feed. That is,

$$\left(\frac{A}{A_0}\right)' = \frac{C_f}{C_b}.$$
(9)

It follows, from eqs. (1), (8), and (9), that

$$R = 100 \left[1 - 2 \left(1 - \frac{a}{r} \right)^2 + \left(1 - \frac{a}{r} \right)^4 \right].$$
 (10)

Equation (10) allows the approximate pore radius to be calculated from the rejection coefficients of molecules of known size. In Figure 8a the rejections to different globular protein at 50 psi of four typical membranes are plotted against the cube root of the protein molecular weight which is an approximate measure of the molecular radius. Figure 8b shows the theoretical curves calculated from eq. (10). The abscissae of both Figures 8a and 8b are comparable since the radius of gyration of albumin is approximately 30 Å.¹⁴ A pore size which appears to be reasonable can be obtained by comparing the two graphs. The result is only approximate and we will show that the retention depends on other factors as well as on molecular size. However, when the membrane water flux and the thickness of the surface layer obtained by electron microscopy are substituted into the Poiseuille equation, a pore size of this order of magnitude is obtained.

In conclusion, these membranes are highly anisotropic, with a "skin" thickness of the order of 1 to 2 microns. The pore radius is less certain but is approximately 10 Å for the most retentive membranes and 100 Å for the most open membranes.

Single Solute Retention

Retention at a Constant Pressure

A series of different molecular weight dextrans, polyethylene glycols, and globular proteins were used to determine the effect of molecular configuration on the relative retention at a pressure of 50 psi. The results are listed in Tables I and II and are shown schematically in Figure 9. In this figure the globular proteins are listed in order of the increasing cube root of their molecular weights, that is, in the order of their approximate molecular radii. The membranes are tabulated opposite the protein which they reject 50%. In some cases the membrane position is interpolated between two proteins. In a similar way the polyethylene glycols and the dextrans are positioned beside the membrane which rejects the 50%. Thus the rejection coefficient of any macromolecule positioned above a membrane is over 50%, and the rejection coefficient of any macromolecule below a membrane is less than 50%. A horizontal line across Figure 9 gives an immediate comparison of the relative retentions of different macromolecules.

Membrane	Rejection R for various solutes, $\%$							
	Globulin M_w 156,000	Albumin M_w 65,000	Pepsin M_w 35,000	Cyto- chrome C <i>M</i> _w 13,000	Insulin M_w 5,700	Bacitracin M_w 1,600		
UM-05			·····		100	100		
UM-2					100	100		
UM-10					100	100		
PM-10				100	100	70		
PM-20			90	70	40	25		
PM-30		100	80	10				
XM-50		100	70	0				
LM-40			80	10				
VM-65		100	60	10				
XM-100	70	10						

TABLE I Protein Retention Data at 50 psi

A Model for the Ultrafiltration Process

Figure 9 and Tables I and II show that all the membranes reject globular proteins much more than linear molecules of the same molecular weight.



Fig. 9. Diagram illustrating the relative retention levels of the membrane with respect to globular proteins and the linear flexible molecules. Molecules are tabulated against the membranes to which their retention would be approximately 50%. Retention coefficient of any macromolecule positioned above a membrane is over 50% and rejection coefficient of any macromolecule below the membrane is less than 50%.

This behavior is the reverse of that found in dialysis and GPC,^{15,16} which also use transport of molecules through microporous capillaries to effect a separation. Craig¹⁷ has reported that with cellulosic dialysis membranes the 50% escape times for a polyethylene glycol ($M_w = 1000$) and the polypeptide bacitracin ($M_w = 1600$) were 2.4 and 1.4 hr, respectively. That is, bacitracin appears to be smaller than the lower molecular weight polyethylene glycol. In ultrafiltration, bacitracin acts as if it is larger than a polyethylene glycol of molecular weight 6000. Similarly, in GPC it is found that linear dextrans are eluted in the same fractions as proteins of twice their molecular weight.¹⁸ Tables I and II show that in ultrafiltration a dextran has the same retention as a protein one-tenth its molecular weight.

In dialysis and GPC, it is believed that relative diffusion coefficients within the barrier media correlate with molecular size. In GPC, Benoit and coworkers¹⁹ have shown that for linear, comb-branched, and star-branched polystyrenes the order of ease of elution of the same molecular weight polymers decreases in the following order: star-branched > combbranched > linear. This is in accord with their solution radii of gyration. In addition, Benoit reduced the elution volume of all three polystyrenes to a universal curve by using their intrinsic viscosities, a measure of the molecular radius in a stationary fluid. Similar correlations have been obtained by other workers with several polymers, including the linear dextrans.^{20,21}

The separation of solute in ultrafiltration takes place in the presence of a solvent velocity gradient due to the movement of solvent relative to the membrane. This results in an extremely large shear rate inside the membrane pores. A flux of 0.2 cm/min in a membrane with a pore radius of 50 Å and a porosity of 50% is equivalent to an average velocity, \bar{u} , of 0.4 cm/min in the pores. The shear rate at the pore wall is then given by

$$\left(\frac{du}{dr}\right)_r = \frac{4\bar{u}}{r}.$$
(11)

For the particular values given above, this results in a shear rate of over 50,000 sec. Therefore, the effect of shear rate on molecular shape has to be considered. The degree of shear-induced deformation will be dependent on the particular macromolecule. We postulate that shear deformation in the membrane pores is the cause of the lower retention of dextrans relative to proteins of comparable molecular weight. Dextrans pass through the membrane because they become deformed by the shear in the pores and have a small cross section normal to the direction of flow. The globular proteins cannot deform and always have a relatively large cross section normal to the direction of flow.

It seems from Ferry's calculations and the treatment of our data that electrostatic forces do not play a major role in the retention of macromolecules by these membranes. This is a serious assumption because of the ease with which polymer molecules acquire charges and also because of the long-range nature of electrostatic interactions. This assumption is in agreement with the result that the order of retention of different macromolecules is independent of the material of which the membranes are made.

Retention as a Function of Pressure

The retention of dextrans in batch cells stirred at a constant rate drops markedly with increasing pressure. This is shown in Figure 10. A similar though not so marked drop in retention with increased pressure is observed with proteins and polyelectrolytes. We believe that this effect is the result of two processes. At low pressures the flux increases with pressure and consequently the amount of shear deformation increases as the pressure increases. The retention therefore falls with increased pressure. At higher pressures the gel layer formed at the membrane surface makes the flux independent of pressure. In this region increased pressure may compress the gel, resulting in a higher concentration of macromolecules at the membrane surface. This also lowers the retention as the pressure increases.



Fig. 10. Rejection of 1% Dextran solutions as a function of pressure using XM-4B membranes.

Retention as a Function of Agitation

In a flow-through cell, increased flow velocity across the membrane surface increases both the retention and the flux. This is shown in Figure 11. In the previous section retention decreased with increasing flux and with increasing concentration polarization. In that section both effects operated in the same direction, whereas here they oppose each other. Increased velocity across the membrane increases the flow rate, which lowers the retention because of increased shear alignment. At the same time, the concentration at the membrane surface is decreased, which raises the retention. Apparently the latter effect is slightly larger. Interestingly,



Fig. 11. Rejection, at 85 psi, of 1% Dextran 110 by a PM-30 membrane in a flow recirculation system. Flux also increases with increased feed recirculation velocity from 0.1 cm/min at 2 fps to 0.19 cm/min at 8 fps.

the same membrane when used in a batch cell has a lower flux and retention than when used in a flow-through cell. This demonstrates the poor agitation in batch cells.

Mixed Solute Retention

Solutions of albumin and γ -globulin were used to study the retention of mixed solutes. The XM-100 membrane has a rejection of 0%-10% for albumin and 60%-80% for γ -globulin when each solute is tested separately, but the results with mixtures of albumin and γ -globulin are



Fig. 12. Diafiltration elution curves of radioiodinated albumin at 50 psi using XM-100 membranes. Pure albumin solution is passed by membrane almost unhindered; however, in the presence of globulin the albumin is retained.



Fig. 13. Diafiltration elution curves of radioiodinated albumin at 5 psi. At this pressure more albumin is passed by the membrane; at the lower solution concentrations, almost complete passage is obtained.

markedly different. A diafiltration technique was used because of the expense of the materials.

Figures 12 and 13 show the elution curves for a tracer sample of radioactive iodized human albumin in a mixture of bovine albumin and Cohn fraction II γ -globulin (at a 4:1 ratio to simulate serum). At 50 psi a 1% albumin solution is able to pass unhindered through the membrane. Under the same conditions a 1% albumin solution with the addition of 0.25% globulin is completely rejected. At lower pressures and concentrations more albumin is passed by the membrane; and at 5 psi, with an 0.05% albumin, 0.025% globulin solution, all the albumin passes through the membrane.

We believe that the gel layer formed at the membrane surface explains these results. The rejected globulin accumulates at the membrane sur-

Concentration of albumin, %	Concentration of globulin, %	Pressure, psi	Retention of albumin, %	Average flux, cm/min				
Pure saline		50	_	1.5-2.5*				
1	0	50	0	0.18				
1	0.25	50	95	0.07				
0.05	0.0125	50	70	0.13				
Pure saline		5		0.3–0.5ª				
1	0.25	5	90	0.07				
0.2	0.05	5	60	0.11				
0.1	0.025	5	30	0.16				
0.05	0.0125	5	0	0.35				

 TABLE III

 Retention and Flux for the Elution Curves Shown in Figures 11 and 13

^a The pure saline permeability is not constant but decreases somewhat at higher pressures because of compaction of the membrane.

face, which lowers the flux and hinders the passage of albumin. The same effect has been used by Kraus et al.²² to separate salt from water. By adding a polymer to a saline solution, he forms a salt-rejecting gel on the surface of membranes which normally do not effect a separation. The globulin gel layer may be overcome by lowering the concentration or the pressure. When this is done, albumin is not rejected. Additional evidence to support this model is given by the flux data in Table III. When albumin is retained, the flux is relatively low. This demonstrates the presence of a gel layer. When albumin is passed, the flux is relatively high.

We wish to thank H. J. Bixler, R. W. Hauslein, B. Keilin, P. Lambert, and A. S. Michaels for much valuable assistance.

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Received April 3, 1969

Revised December 5, 1969