Experiment 14:
Ultrafiltration membranes: Synthesis and permeability studies.

Aim:

1. To test commercial ultrafiltration membranes for separation of hemoglobin from vitamin B_{12}.
2. To form a polyethersulfone (PES) membrane by unsteady state phase separation from a solution of PES in N-methyl pyrrolidone (NMP) on contact with water. To estimate the percent porosity of the membrane.
3. To test the ultrafiltration membrane in a tangential flow module (Millipore Minitan S) for permeability.

Materials and Apparatus:

16% Polyethersulfone (PES) dissolved in N-methyl pyrrolidone (NMP)
Isotonic solution with 0.02 % sodium azide
Vitamin B_{12} 1% in isotonic saline (B)
hemoglobin 2% in isotonic saline (C)
Membrane Casting Apparatus (Fig 5 and Fig 6)
flat glass plate (one side rough)
beakers
Mallet and die
Torque wrench (variable moment)
conical flask (200 ml)
Graduated cylinder (50 ml)--2
clamps
"doctor bar"
glass photograph developing dish
Millipore Corp. Minitan 'S' Cassette (Fig 8)

Brief Background:

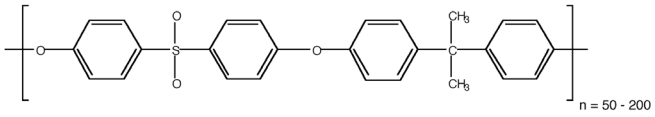
Read the handouts on Polysulfones from Mark et al., "Encyclopedia of Polymer Science and Engineering", vol. 13, pg. 196, and on Membranes, from Mark et al., "Encyclopedia of Polymer Science and Engineering", vol.9, pg. 509. In this lab, we use polyethyersulfone (PES, Victrex).

Forming membranes by unsteady state phase separation:

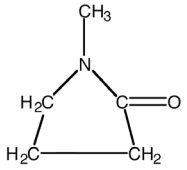
You will use what is called a "doctor bar" to form a uniformly thin layer of a "syrup" on a flat plate. You will then introduce the layer on the plate into a vessel containing water and hold it horizontal as soon as possible. Within seconds or minutes the previously transparent layer of "syrup" will become white. What is occurring is very rapid phase separation, which forms a skin at the water-contacting surface.

The "syrup" contains PES (polyethersulfone) dissolved in NMP (N-methyl pyrrolidone). Their respective formulae are:

Polyethersulfone (PES)



N-methyl pyrrolidone (NMP)



NMP is soluble in water but PES is not. Thus water extracts NMP from the exposed PES-NMP surface, rapidly concentrating the polymer and at the same time precipitating it as a skin, permeable to small molecules but not macromolecules. Water gradually diffuses through this skin and slowly precipitates the underlying PES-NMP, with the formation of micron-size columnar pores. The column-like structure mechanically supports the thin "permselective" skin. (See below micrographs)

{see handout}

Figure 1: Micrographs of ultrafiltration membranes

The denser skin layer and porous support are created by the same process, but the difference in morphology is due to the difference in the rate of precipitation of the polymer. Thus, understanding the unsteady state (time variant) nature of the phase separation process is important in order to understand the process. The following figure is from van den Boomgaard, Boom, Smolders, "Diffusion and phase separation in polymer solutions during asymmetric membrane formation", Makromol. Chem., Macromol. Symp. 39, 271-281 (1990):

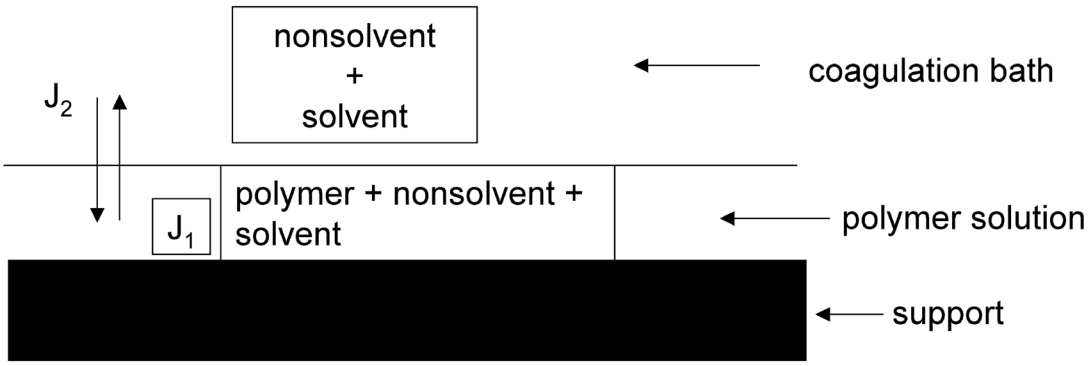


Figure 2. Schematic representation of processes after immersion in a nonsolvent bath; J_1: nonsolvent flux, J_2 solvent flux

Nonsolvent will diffuse from the coagulation bath into the cast polymer solution (J_1) , whereas solvent will diffuse out of the polymer film into the coagulation bath (J_2)

Table 1: Conditions under which an ultrafiltration or microfiltration membrane is obtained.

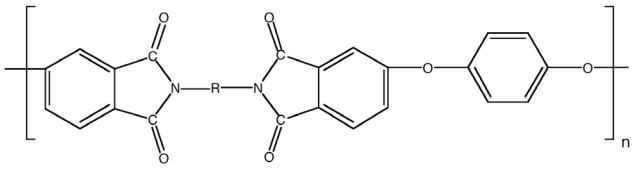
Condition	Membrane & Morphology	Pore size	Utility
$J_2 >> J_1$	UF (ultrafiltration): "skin" of concentrated polymer.	10Å-300Å	Separation of proteins
$J_2 \sim J_1$	MF (microfiltration): visible porosity under SEM.	0.2-0.5 μm	Filter out microbes.

Figure 3 shows how a microporous membrane would look under an electron microscope:

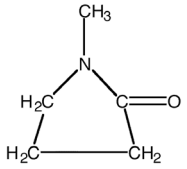
{see handout}

Figure 3: Micrographs of microfiltration membranes.

Figure 4 illustrates how one can change the rate at which the polymer precipitates by changing the composition of the liquid in the bath (the water bath in our experiment). The following results are from an experiment where the polymer solution was a 15% solution of polyetherimide (PEI) in NMP.



PEI



NMP

The y-axis is a measure of the extent to which the polymer has precipitated. The different plots are for different solutions of NMP and water used in the bath into which the cast film is inserted. Note that the process is slowest for the case where the NMP concentration is the highest.

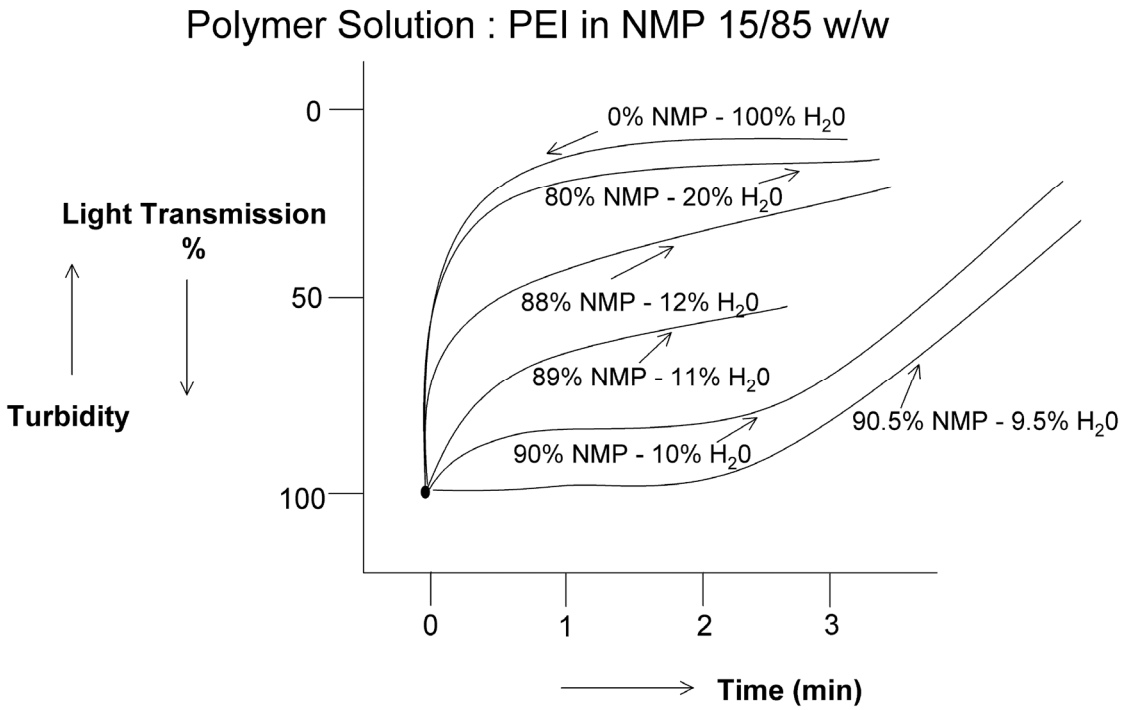


Figure 4: Extent of precipitation of PEI with time as a function of bath concentration

Industrial production of membranes by phase separation:

As industrially practiced, membranes are continuously formed by moving a continuous 36 inch wide sheet of Mylar®, on which the wet lacquer has been cast, into a large tank of water. The Mylar® sheet exits the far end of the tank and the ultrafiltration membrane, formed under water, has sufficient strength so that it can be released from the Mylar® sheet, dried in a warm air oven, and rolled up.

The critical part of this process occurs when the Mylar® sheet with the wet lacquer film enters the water, at about 30 degrees from the horizontal. It is essential to maintain a constant level of water, free of waves or ripples, so that the velocity of entry of the wet film into the water is constant, millimeter after millimeter. A typical industrial production line would operate at 2 to 6 inches per pound.

In the 10.467 lab, we do not have a continuous wet film formation line; we approximate it by a batch process on a 10 - inch glass plate. And instead of the continuous water immersion tank, we approximate the action by sliding the glass plate carrying the wet PES-NMP film under water contained in a glass photograph - developing dish, having the glass plate slide in at approximately 30 degrees. (Our glass plate performs the function of

the Mylar sheet, i.e., as a carrier for the wet film). The water temperature will be either 10 C ± 5 C (cool tap water) or 40 C ± 5 C (warm tap water), as specified.

Precautions:

Avoid skin contact with NMP. Use vinyl or nitrile gloves.

Procedure:

A. Formation of a wet film of PES-NMP using a doctor bar:

1. The following procedure is to be repeated a few times so as to obtain at least two good films from the 16 % PES solution.
2. Set the doctor bar on the glass plate's rough side with 0.007 inch clearance down, so gap is 0.007 inch (fig 5-side view). Snap in the aluminum guards (fig 5-top view) so that a rectangular reservoir is defined between it, the glass plate, and the doctor bar. Attach the end guide (fig 5-top view) with a 1/4-20 machine screw so that as the end guide slides along the 10 inch side of the 8 X 10 glass plate, the doctor bar moves at 90 degrees to the 10 inch side. Start with the doctor bar close to an 8 inch side of the glass plate. (see fig 5-side view)
3. Dispense about 20 ml of the PES-NMP solution into a beaker. Then from the beaker pour the solution slowly and uniformly into the rectangular reservoir (see fig 5-top view). Avoid entraining air.
4. Place paper towels under the far end (8 inch wide end) to catch excess solution. Move the doctor bar with a uniform motion about 1 inch per second, so that it spreads the solution over the glass plate as a uniform layer. Keep moving until the doctor bar, guard, and end guide go off the glass plate and onto the paper towels.
5. The PES-NMP liquid film on the glass plate is now ready for conversion to membrane by immersion in a tray of water as shall be discussed in section B to follow.
6. The doctor bar and its attachments are cleaned up under running water which precipitates the PES. The NMP is safely discharged in the waste water. When the glass plate is retrieved from the tray of water, the membrane will have floated cleanly off.
7. Thoroughly dry the glass plate, the doctor bar, aluminum guard, and end guide before forming the next wet film by the procedure in the first two paragraphs above.
8. The solution that is caught on the paper towels should be precipitated by flushing the towels under running water. Wring out excess water and dump in waste basket.

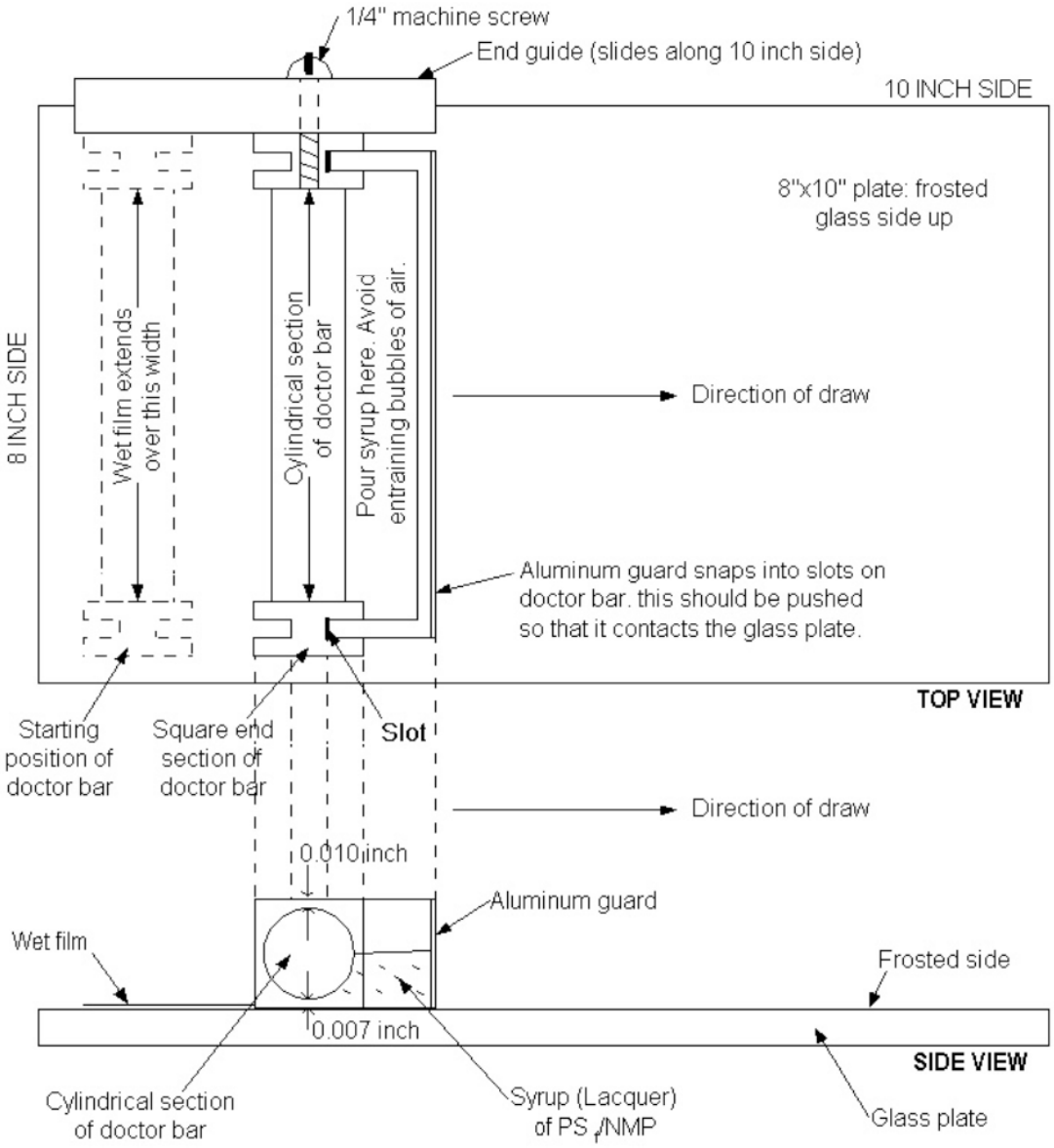


Figure 5: Membrane casting apparatus

B. Formation of a membrane by immersion under water:

1. Take the glass plate carrying the PES-NMP film under water contained in a glass photograph-developing dish while having the glass plate slide in at approximately 30 degrees. (See figure 6) Try to avoid creating water currents when sliding the glass plate into the water.

2. Perform the above experiment for each concentration of PES while maintaining the water temperature at 10 ± 5 C (cool tap water) or 40 ± 5 C (warm tap water).

3. Estimate the time after immersion required to obtain uniform opaque white color. The membrane will spontaneously release from the plate. Transfer it to a bucket of tepid water and let stand for 20 minutes.

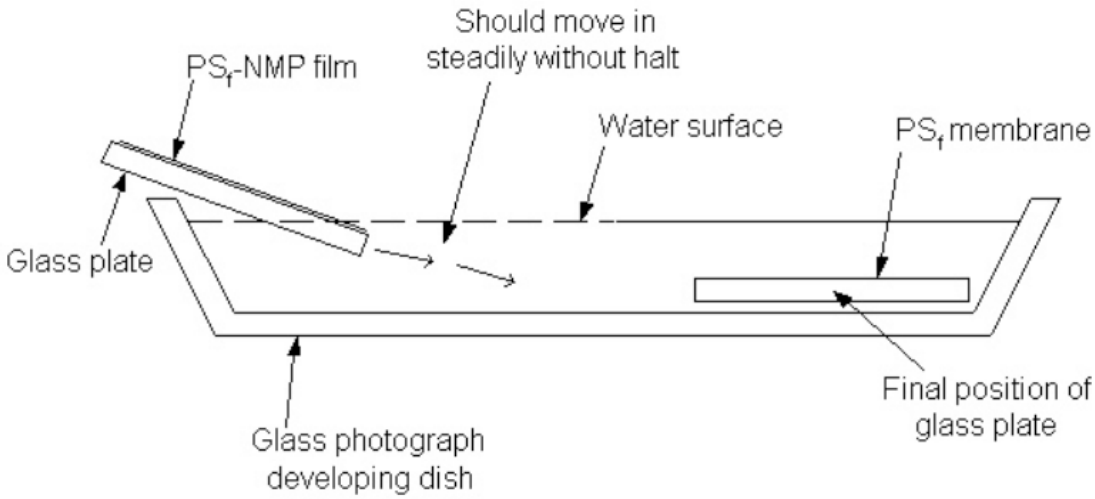


Figure 6: Immersion of the glass plate into the water bath

C. Thickness/weight measurements & preparation for ultrafiltration experiments:

1. Use two different casting temperatures:
   a) 10°C, (cool with ice cubes, remove cubes before casting)
   b) 40°C, (hot tap water may be sufficient; otherwise, add boiling water to bring up to 40°C. ***Stir in both cases to make uniform in temperature.***

Measure membrane thickness (see notes)

2. If you have achieved defect-free sheets (no bubbles, pinholes, other irregularities) you should cut out using mallet and die rectangular membranes to fit the Millipore Minitan S module. What you need is at least one viable membrane of each type to fit in the Minitan-S unit.

3. Place your membrane on a Teflon cutting surface. Position the rectangular cutting die on the membrane. Hit the wood block on top of the die. Cut out the two guide holes with a razor blade. (Figure 7)

4. After die-cutting your membrane, use the dial micrometer to measure thickness on the scrap material at several places along the short and long sides from which the rectangular membrane was removed. Record these readings for each membrane. Store you

die cut membranes, carefully labeled in distilled water containing 0.02 % sodium azide, in preparation for the ultrafiltration experiment.

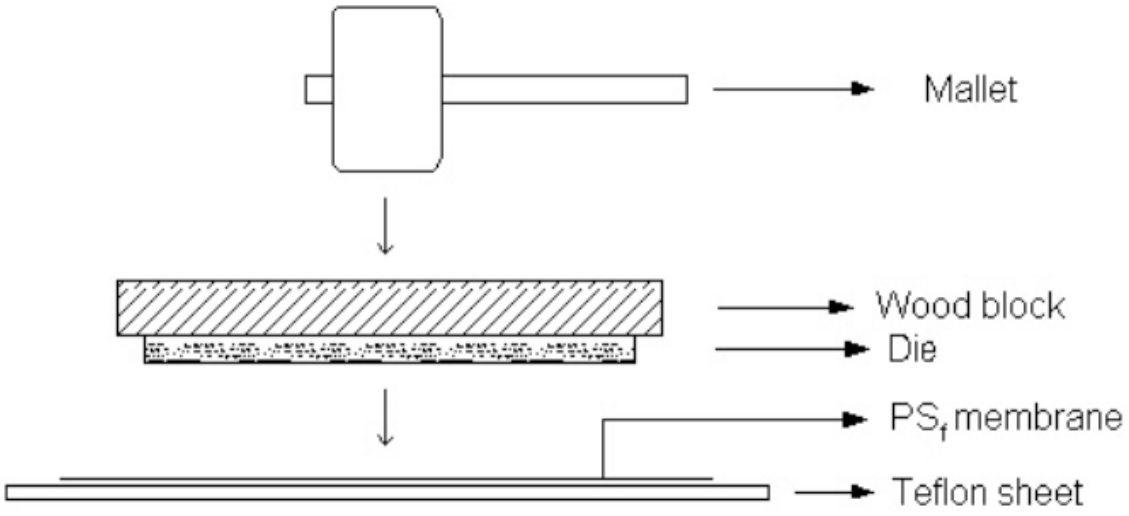


Figure 7: Using the die to cut the membrane

D. Ultrafiltration experiments:

1. Installation of the Millipore Minitan-S module: (See figure 8)

a) Remove the four nuts and washers from the filter holder.

b) Remove the top plate and manifold.

c) Thoroughly wash and dry two retentate separators.

d) Place a clean retentate separator on the bottom manifold.

e) Place your membrane shiny side down over the retentate separator.

f) Install the upper manifold with the grooved side down against the dull side of your membrane.

g) Install the top steel plate. Replace the four washers and nuts. Simultaneously, finger-tighten diagonal pairs of nuts. Continue tightening the nuts by using a torque wrench as follows: **(i)** Set the torque wrench to 20 in-lbs by sliding the collar back, and turning the wrench handle until the line corresponding to 20 in-lbs on the barrel aligns with the zero reading on the sleeve die. **(ii)** Place the wrench socket over one of the nuts and rotate the nut clockwise, 1/8 of a turn. Starting with the nut diagonally across from the first nut, tighten the other nuts in the same manner. Repeat the cycle until each nut is tightened to the specified torque. The wrench will make a "clicking" sound and will give slightly when the

torque is achieved. **(iii)** Set the torque wrench at 50 in-lbs and repeat step (ii). **(iv)** Set the torque wrench at 80 in-lbs and repeat step (ii).

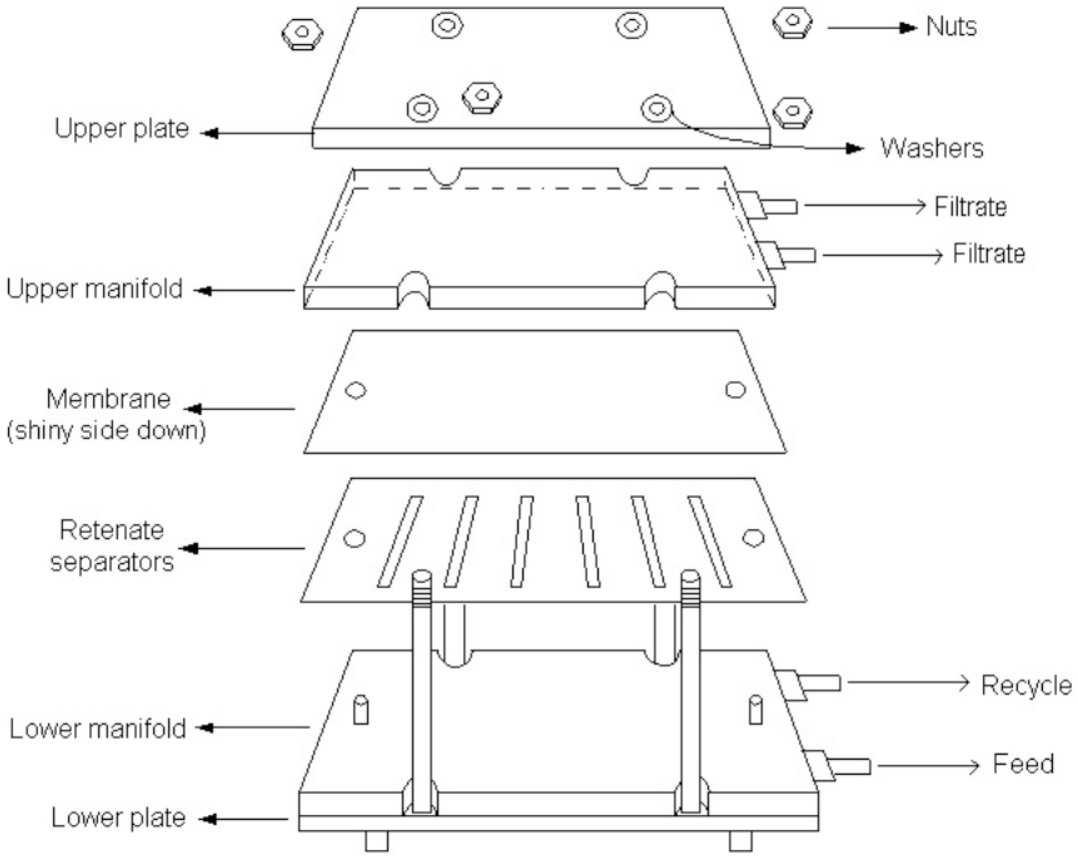


Figure 8: Installation of the Millipore Corp. Minitan-S module

2. Operating instructions for the Millipore Minitan-S module:

a) Place the pump feed line in a 200 ml flask of water.

b) Attach a pressure gauge to the line connecting the pump and the filter module.

c) Place the filtrate lines in a 50 ml graduated cylinder.

d) Place the recycle line in another 50 ml graduated cylinder. Attach a clamp to this line.

e) Adjust pumping speed and recycle rate (with clamp) to achieve a pressure of 2.5 psi.

f) Measure the filtrate flux rate and recycle rate in ml/min.

g) Increase pressure to 50 psi. Repeat step (f).

h) Decrease pressure to 25 psi. Introduce blue Dextran/yellow food coloring solution into the feed flask. Repeat (f) and (g). Note color of filtrate.

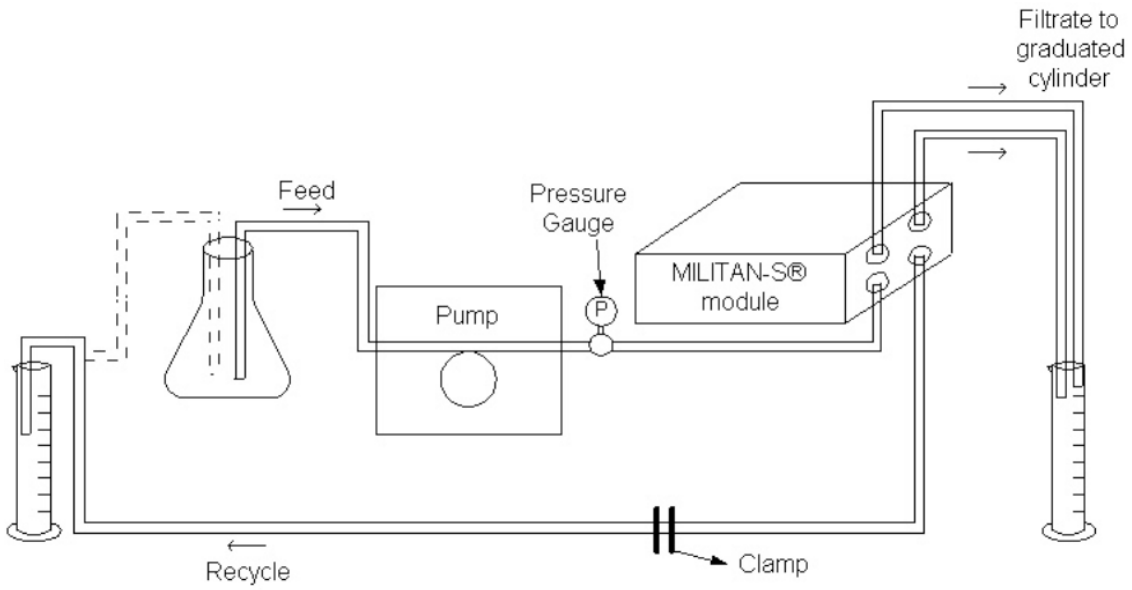


Figure 9: Final set up for permeability studies

Ultrafiltration Part (a) – Commercial Membranes

Ultrafiltration Experiments using Minitan S Module:

Solutions: **A** 0.9% M NaCl in water (isotonic solution)

B 0.9% M NaCl in water + 1% vitamin B_{12}

C 0.9% M NaCl in water + 2% hemoglobin

E. Permeate flux Millipore Corp UF membrane "PTGC", nominal 10,000 mol wt cut-off

Using only Solution A, measure the permeate flux rate (ml/min) as a function of trans-membrane pressure ΔP and recycle rate (pump speed). The recycle can be measured volumetrically (ml/min).

F. Concentration by ultrafiltration

Replace Solution A by 100 ml of Solution C in the reservoir. Set ΔP at 30 psi, using a pump speed about halfway between max and min.

Continue ultrafiltration until 50 ml of clear permeate has been recovered. Record permeate flux rate (ml/min).

G. Constant volume washing

Add 50 ml of Solution B (Vit B_{12}) to the reservoir containing the concentrated hemoglobin (now about 4%). Swirl to mix.

Now add 500 ml of Solution A to the reservoir. Run at ΔP = 30 as above. Collect the permeate in 50 ml aliquots, serially. Observe how the color (Vit B_{12}) diminishes. Record permeate rate (ml/min).

Ultrafiltration Part (b) – Lab-made membranes

(1) Use the membranes made from 16% w/vol VICTREK 5200G Polyethersulfone in N-methyl pyrrolidone on day 1.

(2) Cut out your membranes (10^oC membrane, 40^oC membrane) Install in Minitan S (one membrane at a time). Measure permeate flux rate at ΔP = 30 psi, for each membrane, for Solution A (isotonic solution).

(3) If you achieve a significant permeate rate for the 40^oC membrane, replace Solution A by Solution C (50 ml) and restart the ultrafiltration. Determine whether or not hemoglobin appears in the permeate.

Observations and Calculations:

1. Part B: For each membrane, record the time after immersion required to obtain uniform opaque white color.
2. Part C: Record thickness of the membranes.
3. Part D: Record for each case - pressure, pumping speed, recycle rate, filtrate flux rate. Also make qualitative observations on filtrate color or other problems.

Discussion:

1. Discuss your results in light of the background theory. In particular, what kind of a membrane do you expect? What did you get? How can you tell? In very simple terms discuss permeability and selectivity of your membranes.
2. What was the role of temperature in membrane structure and formation? Explain your observations, and what your expected results would be.