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FILTRATION AND ULTRAFILTRATION EQUIPMENT AND TECHNIQUES

John Pellegrino[a]
[a] Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, CO, U.S.A.

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FILTRATION AND ULTRAFILTRATION EQUIPMENT AND TECHNIQUES

John Pellegrino

Physical and Chemical Properties Division,
National Institute of Standards and Technology,
Boulder, CO 80303

ABSTRACT

The spectrum of filtration separations runs from the millimeter scale (beach sand and activated carbon particles) using coarse filters, to the angstrom scale (metal ions and gas molecules) using reverse osmosis or gas separation membranes. Between there are microfiltration (bacteria and emulsions), ultrafiltration (proteins, viruses, and colloids), and nanofiltration (sugars, herbicides, small organic molecules). In the analytical environment it is likely that membrane and filtration systems involving this entire spectrum will be used to provide high purity water, gases, reagents, and even special functions within instruments. In addition to these applications, membranes and filters will often also be used in sample preparation and perhaps initial characterization. In this entry, we

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will discuss the principles, materials, and devices used to accomplish coarse, micro- and ultrafiltration on the laboratory scale.

INTRODUCTION

A membrane is defined as a structure that has lateral dimensions much greater than its thickness and through which mass transfer may occur under a variety of driving forces. With this viewpoint many materials, commonly called filters, may also be considered membranes. As a working differentiation between filters and membranes, filters will be considered as those materials whose lateral dimensions are not usually = 100x greater than their thickness and whose separation function is primarily by capture of species (or particles) through its depth.

BACKGROUND

Figure 1 presents a schematic of the target solute sizes in the various membrane and filtration forms.

The general performance measures for filtration and membrane separations are speed, selectivity, and stability.

- Speed is how fast you can process a specified volume of fluid.
- Selectivity is how well the membrane (or filter) discriminates between the components of the feed stream presented to it.
- Stability is how long the two previous performance measures retain their initial (presumably desirable) levels.

All three of these performance measures depend on the physical and chemical properties of the membrane (filter) and the feed stream being processed, as well as on the contacting device that is being used. In general, there is always a trade-off between recovery of components in the feed stream (solvent or solutes) and the purity obtained, and some measure of cost—but improvements in materials and equipment have consistantly lessened that trade-off.

Materials and Formation Techniques

Membranes and filters are formed by a variety of methods and from numerous materials both of which profoundly influence the structure and morphology of the resulting product. It is important to realize that all formation techniques and materials are not interchangeable, and in fact, many are mutually exclusive. Membrane and filter materials include those listed in Table I. The general formation techniques include those presented in Table II.

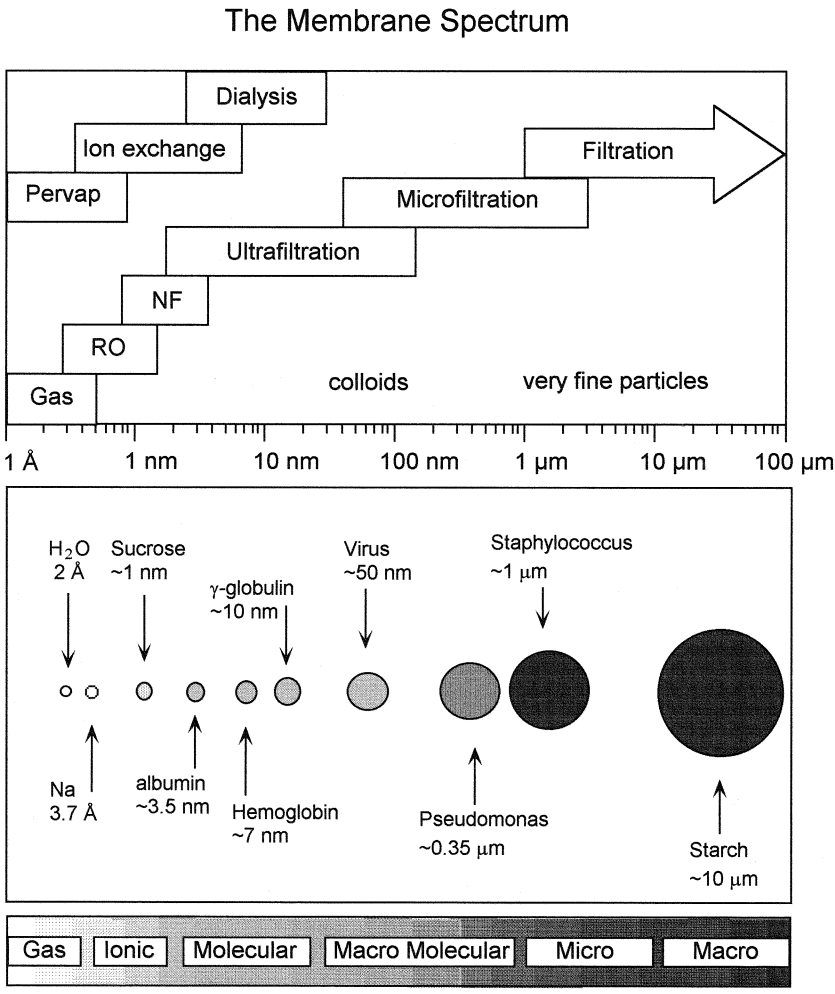

Figure 1. Schematic of the filtration spectrum. (Courtesy of Michael D. Guiver and Chung M. Tam, National Research Council of Canada.)

General Terminology and Definitions

Membrane and filtration technology has developed a specialized terminology. The definitions themselves provide a basis for discussing the equipment and operating principles. The following list includes many items that will be discussed further in later sections of this chapter.

Table I. Membrane and Filter Materials

Inorganic	Inorganic - Organic	Organic
• glasses • ceramics • metals • polymers	• ion-containing polymers • polysiloxanes • polyphosphazenes	• natural polymers polysaccharides polypeptides rubbers • synthetic polymers thermoplastics rubbery polymers soluble linear insoluble crosslinked

- *Batch Filtration*: A fixed volume of feed material is filtered with the retentate (the feed material not filtered) recycled (or not removed) until a specific recovery of permeate is obtained. Thus the composition of the feed is continuously changing with time.
- *Cake*: The cake is whatever is left sitting on the membrane or filter's surface (or whatever builds up continuously during the filtration).
- *Concentration Polarization*: Accumulation of rejected solute on the feed side of the membrane or filter surface, excluding cake or adsorbed lay-

Table II. Formation Techniques of Membranes and Filters (Examples are in Parentheses)

Fibers	Particles	Films
• wet-lay (many paper filters) • dry-lay (spunbonded olefins) • wound (glass filament cartridges) • woven (polymeric and/or metal filter meshes)	• sol-gel (ceramic ultrafilters) • compression or sintering (metal and glass filters and frits) • extruded (alumina microfilter monoliths)	• extruded dense films (silicone films) • extruded and stretched dense film (teflon and olefin microfilters) • cast or extruded films with phase inversion step (cellulose acetate ultrafilters) • nuclear-particle track etched (polycarbonate microfilters) • electrochemical deposition (homoporous alumina microfilters)

ers. Interrupting or stopping the filtration process allows the concentration polarization to dissipate.

- *Conductance*: The reciprocal of resistance. The flux (see below) of solvent (or solutes) through a membrane is often empirically described as being proportional to the product of a driving force and a conductance. Several layers with different thicknesses and specific conductances (conductance normalized by its thickness) may be combined to completely describe the membrane system under a variety of conditions.
- *Crossflow (tangential flow) Filtration*: The main flow direction is across (tangential to) the membrane or filter surface. This operating mode will typically have a retentate.
- *Dead-End Filtration*: The main flow direction is perpendicular to the membrane or filter's surface. This operating mode may or may not have a retentate.
- *Feed (or Sample)*: The initial solution presented to the membrane or filter is called the feed. It can be a mixture of solvent, solutes, and particulates.
- *Fluid Velocity (Crossflow Velocity)*: The averge velocity in the feed channel in a flowing system or the average radial velocity across the membrane or filter's surface in a stirred system.
- *Flux*: The mass or volumetric flow through the filter/membrane per unit time per unit area.
- *Fouling*: Irreversible decline in flux due to adsorption, deposition, or other accumulation on the surface and/or in the pores of the membrane or filter. This can be caused by any combination of solutes, particulates, and precipitates.
- *Hydraulic Pressure Drop*: In a flowing system this is mechanical pressure required to move the feed through the device to become the retentate. It is mechanical energy required in addition to the average TMP (see below). The viscosity of the feed solution and shape of the feed channel (including any inserts to increase mixing) will affect this energy requirement.
- *MWCO (Molecular Weight Cut-Off)*: The molecular mass of dissolved molecules for which a rejection of at least 90% will be observed based on the measurement technique and assumptions used by the manufacturer. A standard measurement technique does not exist.
- *Particulates*: These are species that are suspended in the primary solvent or continuous phase. Particulates can include colloids, cells (and cell fragments), viruses, spores, inorganic precipitates, dust, etc.
- *Permeability*: The permeance (see below) normalized for the thickness of the membrane or filter's separating layer.
- *Permeate (Filtrate, Product)*: Permeate refers to whatever passes through the membrane.

- *Pore Size*: The diameter of the largest pore based on the measurement technique and assumptions used by the manufacturer. A standard measurement technique does not exist.
- *Permeance (Pressure-Normalized Flux)*: The flux divided by the TMP.
- *Permselective*: A membrane is permselective towards a feed mixture if the concentrations in the permeate differ from the feed.
- *Recovery*: Percentage of the feed that permeates a single filtration stage. A stage may be an element, device, or module in which there is no interruption in the contact of the feed solution and the membrane or filter.
- *Rejection*: A measure of the fraction of solute or particulate retained by the membrane or filter. Several rejection quantities (e.g., true, observed, and average rejection, and sieving coefficient) are defined and used.
- *Retentate (Concentrate, Reject)*: Retentate is the fluid feed material that does not pass through the membrane or filter
- *Solutes*: These are species that are dissolved in the primary solvent or continuous phase. Solutes can include salts and both small and large molecules of a variety of types.
- *Transmembrane Pressure (TMP)*: The difference in absolute pressure across the thickness of the membrane or filter is called the transmembrane pressure. Depending upon the type of filtration operation this can change with position along the surface of the filter. Also it can result from a variety of sources, such as inert gas blanket, pumping, and centrifugal force.

Characterization

The most common parameters used to characterize membranes and filters fall in three general categories (see Table III). These are transport properties, pore (geometric) characteristics, and surface (or predominantly chemical) properties. There is actually a considerable dependence of transport properties on the pore and surface characteristics, but no general predictive capability yet exists.

Table III. Categories of Membrane or Filter Characterization

Transport Properties	Pore Size Characteristics	Surface Properties
• solvent flow (hydraulic permeability) • solute or particle rejection (sieving coefficient) • solute diffusion	• pore size distribution • pore shape • pore morphology gradient through membrane thickness	• chemical composition • hydrophobicity - hydrophilicity • surface charges • solute-membrane affinity • surface texture

Additionally, users may also require membrane or filter characterization with regards to chemical compatibility in a specific application (environment). As a first step, pH, solvent, and temperature resistance tabulations for the nominal material composition may be consulted.

It is important to note that most reported data on membrane properties will be dependent on the test protocol used. There is not widespread consistency among manufacturers with respect to characterization techniques. Therefore membrane users may encounter unexpected performance differences between materials, nominally similar, but supplied by different sources. These issues will be discussed further in later sections of this chapter.

In the laboratory environment a variety of membrane and filter contacting devices will be encountered. There are key details of the device design and membrane morphology that will affect observed performance regardless of how the system may be "packaged." These differentiating criteria will include:

- Operation in dead-end (with or without stirring) or cross flow mode.
- Full or partial recovery of the feed mixture.
- Application of an external transmembrane pressure via pumping, inert gas blanket, or evacuation of the permeate side of the device.
- Use of flat sheets (either singly or multiply), hollow fiber bundle, or tubular membranes.

MODES OF USE

Successful use in a variety of applications results from appropriately coupling filtration and ultrafiltration materials, equipment, and operating conditions. Though the end-use objectives will vary widely, the general principles apply broadly. The following are some general categories of use.

Analysis

For analytical uses there are many possible objectives including:

- Ion or gas selective electrodes using membranes made from glasses, crystals, metals, polymers, solid polymer electrolytes, immobilized liquid membranes, and derivatized porous membranes. The electrochemical reaction that "senses" the analyte is usually subject to interferences. The membrane's purpose is to very precisely control the transport of specific species. The rate of transport will be proportional to the concentration at the feed side of the membrane.
- Sampling systems for collection and analysis of contaminants, including microbiological, particulate, colloidal, or airborne. For example, ultra-

filtration membranes are used for collection of natural organic matter from surface waters.

- Membrane or filter collection of target analytes, for example, as blotting membranes in biochemistry and ashless collection filters for use in quantitative analysis.
- Membrane interfaces for mass spectrometers provide attenuation of the total mass load fed to the high vacuum chamber. This attenuation can be either mass selective or not. An example of the former is that a highly hydrophilic membrane can be used in a micropipette probe, which is selective for water (most likely deuterated) transpired by an organism in an ambient environment. In this case, atmospheric gases would essentially be excluded from the mass spectrometer.

Concentration

The desired result is to remove solvent from the feed mixture. This is easily accomplished. The trade-off is usually between the size of equipment and processing time.

Dehumidification

The purpose is to remove water from a pressurized gas stream. A membrane with a high water affinity is used as a mass transfer barrier. A depressurized portion of the retentate stream (dehumidified feed) is used to "sweep" the water permeating the membrane.

Flow (Mass Transfer) Control

The objective is to use the predictable transport characteristics of a well-chosen membrane structure to deliver material at a controlled rate to an instrument. Examples include membrane inlets for mass spectrometers (though note must be taken of the potential separation of a feed mixture due to differential Knudsen diffusion rates of the components) and vapor permeation tubes to provide calibration standards for gas chromatography.

Fractionation

The purpose is to recover multiple components of a complex feed mixture. To accomplish this one would usually need to apply multiple filtration stages,

each one subject to the trade-off between recovery and purity. Certain fractionations may be accomplished with a single membrane by varying the solution conditions (pH, ionic strength, TMP, fluid velocity, etc.). To accomplish efficient fractionation the properties of the membrane and the process conditions must be chosen very carefully.

Humidification (and Gas Dissolution)

The purpose is to saturate a gas stream with a vapor (usually water). This can be done with a variety of membranes and contactor designs. The same principles and equipment can be used to accomplish the inverse objective—saturating a liquid stream with a gas, such as in a blood oxygenation. Often a membrane that is nonwetted by the liquid phase is used, but denser films will also work.

Purification

The purpose is usually to remove some feed component(s) completely or to recover one feed component in a very pure form. These objectives cannot easily be achieved in a single membrane or filtration stage (especially with high recovery) unless there are some very large physical or chemical property differences. An exception is the use of the general class of affinity membranes. These contain chemical groups for specific adsorptive binding.

Salt Removal (or Buffer Exchange)

This is typically done by either dialysis or diafiltration, defined in the following.

- Dialysis requires diffusion of the small molecules through a permselective membrane that will not allow passage by diffusion of the other constituents of the feed. This membrane requirement can be relatively easily achieved. The concentration of the target molecule in the feed decreases with time as does its rate of transport. Thus the efficiency of removal is also decreasing.
- In diafiltration the target small molecule flows through a membrane in convective flow. The volume of permeate is continuously back-added to the feed with pure solvent. The efficiency of removal can be very high, but the properties of the membrane and the process conditions must be chosen very carefully.

Solute Recovery

The desired product is either a dissolved solute(s) or a suspended particulate (from a precipitation) or a colloid. The recovered solute may either pass through the membrane or be retained in solution or on the membrane or filter's surface. Typically if ~100% recovery is targeted, then purity will be sacrificed. The trade-off between these two will depend on almost every variable that describes the membrane system.

Sterilization

The purpose is the removal of micro-organisms, virus particles, and other pathogens. This is a special case of a purification application but a very widely (and successfully) used one.

TYPES OF DEVICES

Funnel

The simplest and most familar contacting devices are variations on the funnel theme (Fig. 2). The driving force for mass transfer can be a combination of the liquid height (hydrostatic head) above the membrane's surface and a vacuum applied on the permeate side of the membrane. When a vacuum is applied, the rate of filtration will be more constant than otherwise and it will be possible to recover essentially all of the feed liquid as permeate. When using a vacuum, a phase change of the permeating fluid can occur within the pore structure of the membrane or filter. This can result in a change in permeation rate versus what would otherwise be expected. This type of device is useful for treating small volumes of feed to either recover suspended solids or provide a "filtered" permeate. Cake buildup on the surface, and/or pore plugging, will eventually result in the inability to filter any further volume due to insufficient TMP.

In-line Filters

Syringe filters are a special case of in-line filters. Gas venting filters are also included in this category. Figure 3 presents a generic, reusable in-line filter housing that allows disassembly and replacement of the filter or membrane. These types of contacting devices operate by dead-end filtration. The driving force for mass transfer is the mechanical pressure provided on the fluid at the feed side. This driving force can be applied by physical force on a plunger (variable) or by

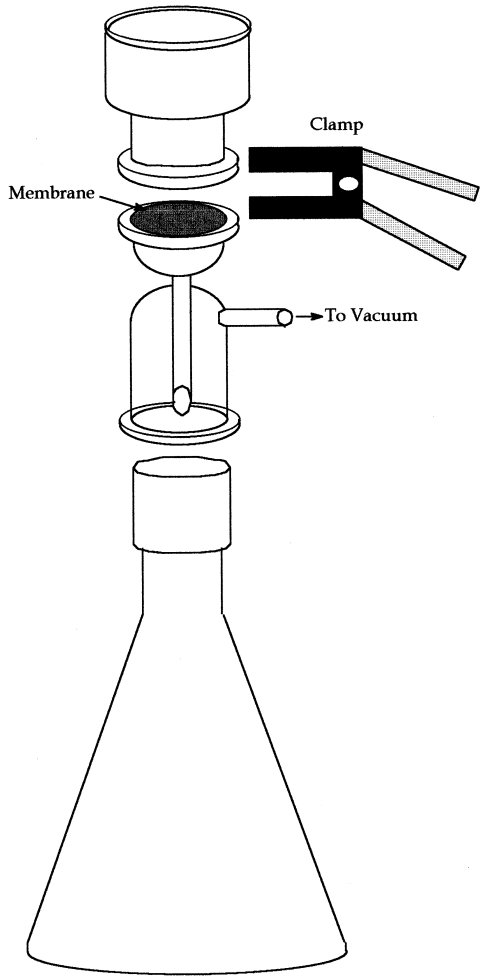

Figure 2. Typical funnel filtration assembly. A similar operating approach is also incorporated into integral, two-chamber filtration units. These are usually made out of plastic and can be both reusable, sterilizable, and/or disposable.

a pump (constant). These filters or membranes are available as either replaceable elements for a reusable housing (pressure vessel) or in self-contained disposable housings. This type of device is useful for treating both small and larger volumes of feed (gas and liquid phases) in either batch or semi-continuous operation. The objective will mainly be to provide a "filtered" permeate. Cake buildup on the surface and/or pore plugging will eventually result in the inability to filter any further volume due to insufficient TMP.

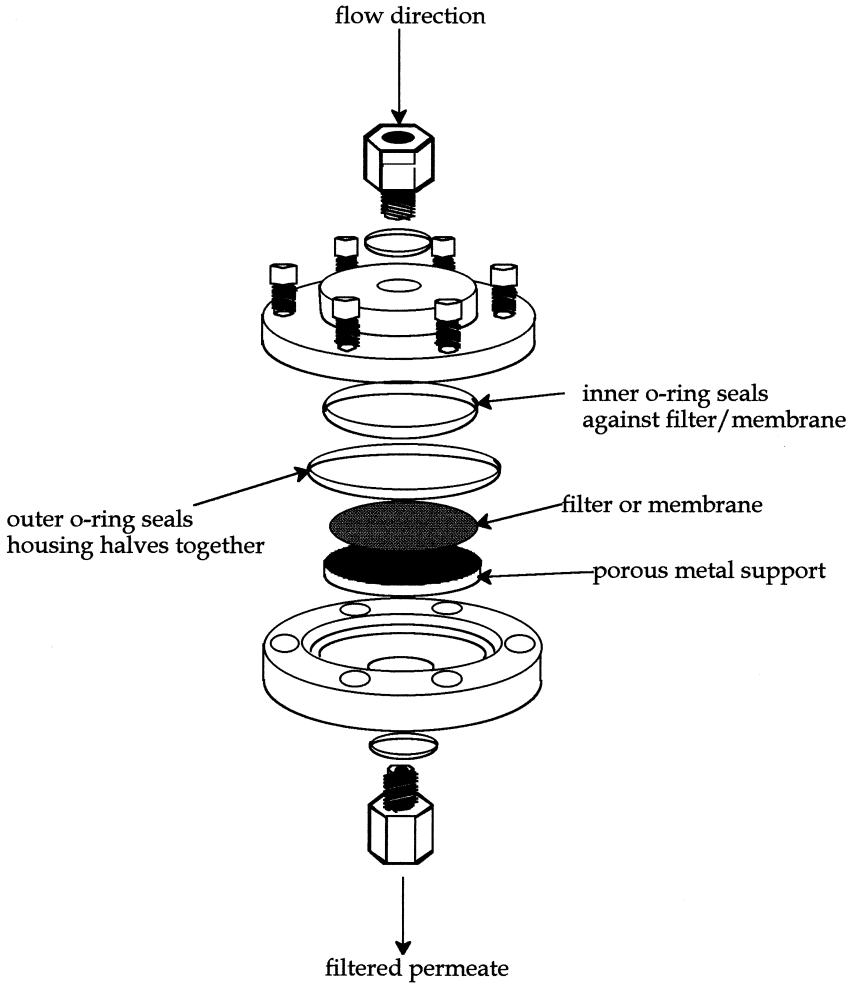

Figure 3. Generic, reusable in-line filter holder. Many different designs exist with respect to materials of construction, pressure rating, inlet and outlet fittings, and how the two halves of the housing are connected. Such a housing is useful for gases, liquids, and vapors.

Centrifuge Tube Devices

Centrifugal forces can be used in place of a pump or inert gas blanket to provide TMP to perform filtration. A variety of devices have become available that place a membrane between a feed and permeate collection volume. The designs include membrane inserts for microcentrifuge vials (Fig. 4a), as well as, self con-

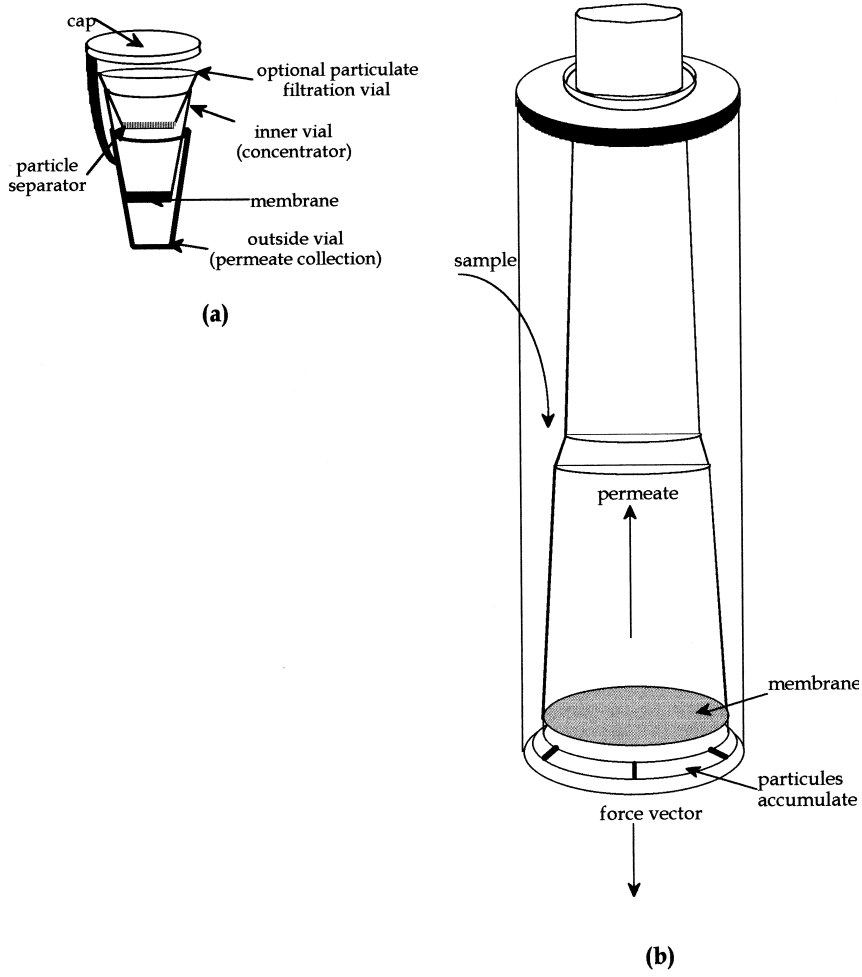

Figure 4. (a) Schematic of microcentrifuge tube design including a particle separation followed by membrane filtration. (b) Schematic of a prep-scale (~15 mL starting volume) centrifuge tube design in which fluid is forced through the membrane filter above a level where particulate sedimentation occurs.

tained devices with novel approaches to minimize fouling and pore plugging (Fig. 4b). The entire unit is placed in a centrifuge and the force vector drives permeate through the membrane or filter. Membranes are available for rejection of species from particulate sizes down to small macromolecules. Centrifugal forces (500 to 14 000 × g) and duration of spinning (1 min to 1.5 h) vary depending on the particular device and feed mixture. The devices are designed to accommodate small

sample volumes from 20 μL to 20 mL. It is a dead-end filtration designed to recover a "filtered" permeate. Concentration polarization, cake buildup, and/or pore plugging may eventually result in the inability to filter any further volume due to insufficient TMP.

Diffusion Devices

These devices are typically tubular membrane sleeves that can be filled with a solution and clamped at both ends. The filled tube is then immersed in a large vessel containing another fluid. Permselective diffusion between the two fluid phases is controlled by the membrane's properties. Either fluid phase can be periodically replenished or changed during the processing cycle. These devices will typically be used to perform batch dialysis.

Stirred Cell Modules

This design (Fig. 5) uses a stirring bar situated close to the top of the membrane or filter's surface to decrease the rate and extent of concentration polarization and/or cake buildup during the filtration process. The TMP is typically supplied by an inert gas blanket. Maximum operating pressures are usually from 0.6–0.9 MPa. The designs can accommodate feed volumes from as low as a few microliters to several liters. This module design is typically a dead-end filtration operation. The general purpose is to provide faster processing times and longer membrane usage without needing to provide the additional equipment (pumps, etc.) for a crossflow module. Also shear sensitive solutes will probably spend less time under stress in this type of design than in a crossflow design. It is possible to run several sequential batches using the same membrane and relaxing the TMP in between the batches.

Crossflow Modules

Crossflow modules have a wide variety of designs. They can use either flat sheet or hollow fiber membrane forms. If based on flat sheets, then the modules may contain a single membrane or multiple membrane leaves. Modules for multiple membrane leaves can be either plate-and-frame or spiral wound approaches. Plate-and-frame modules can be obtained with individual, user-removable spacers, gaskets, and membranes, or cassette designs where the membrane leaves,

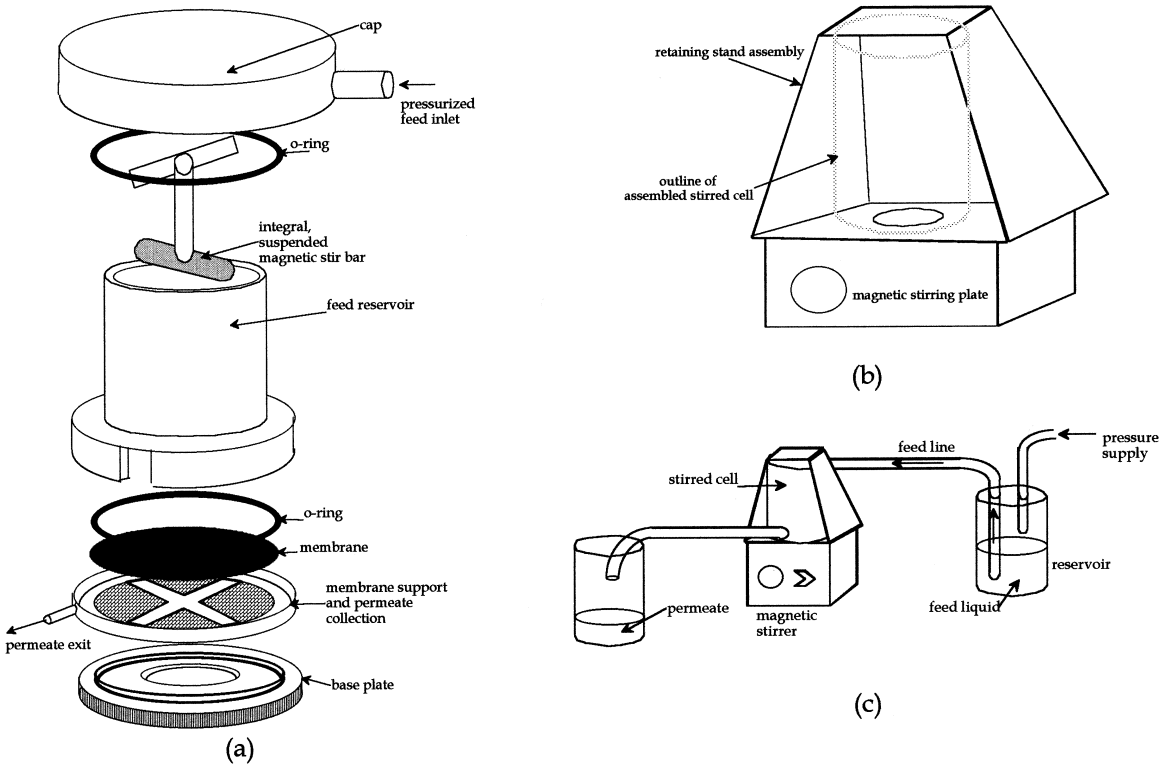

Figure 5. (a) Expanded-view schematic of a stirred-cell membrane filtration assembly. (b) An external housing provides the clamping pressure to keep assembly together on top of a magnetic stirrer plate. A cut-out in the external housing facilitates good coupling between the magnetic stirrer and the unit's internal stir bar. (c) A typical process configuration for batch filtration using an inert gas blanket on the feed reservoir to provide the TMP.

spacers, etc. are all sealed together by the manufacturer and replaced as a unit (Figs. 6 and 7). Spiral wound modules are pressure vessels that use replaceable spiral wound elements. This design is not commonly encountered in laboratory applications other than for producing ultrapure water. Hollow fiber devices (Fig.

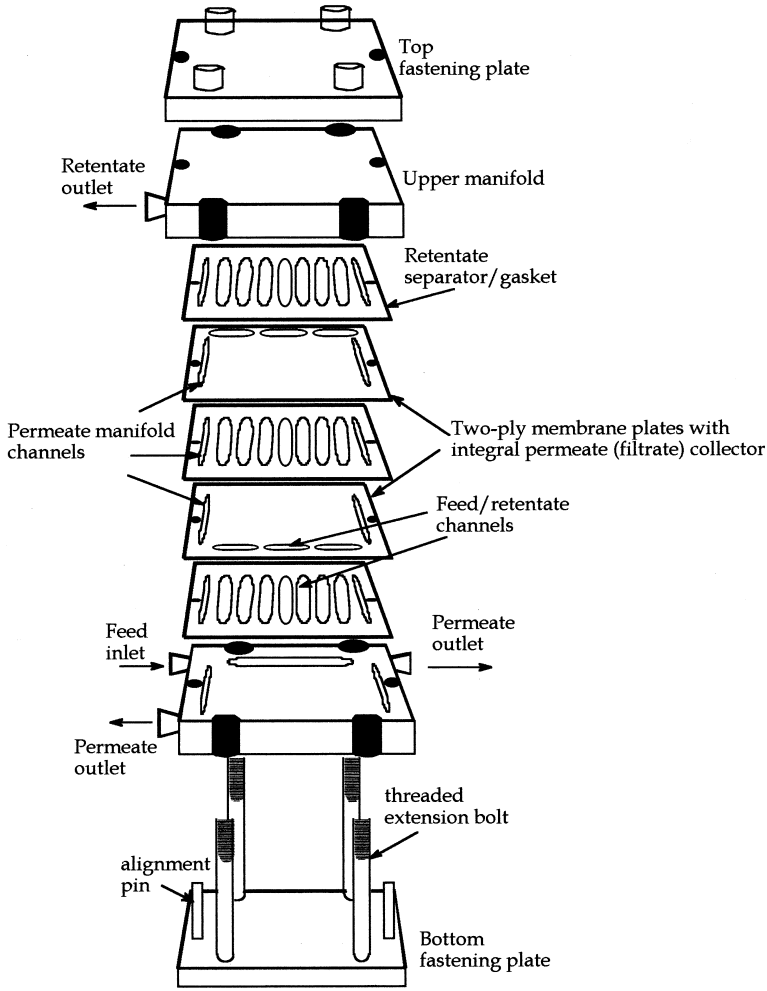

Figure 6. Expanded-view schematic of a plate-and-frame type crossflow module. A variety of designs exist, including those which use separate membranes and permeate spacers instead of the two-ply membrane plates with an integral permeate spacer shown here. Note that the feed/retentate channels are part of the gasket that seals the membranes in place and separates the permeate header (channel) from the feed fluid.

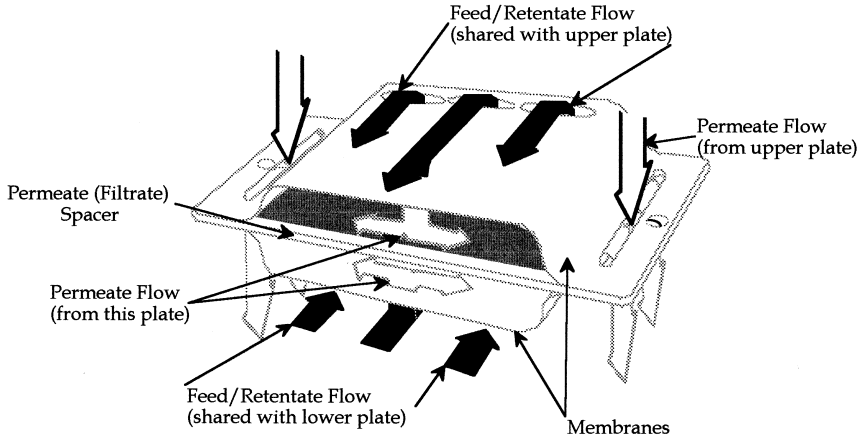

Figure 7. Schematic of a two-ply membrane plate with integral permeate (filtrate) spacer. The feed flow is directed parallel to the membrane surface and moves up and across successive membranes until the unfiltered-retentate leaves the module. A permeate spacer is sealed between two membranes. This spacer can be sealed to the membranes by an adhesive, heat-bonding, or special gaskets and clips. The permeate spacer directs the filtrate to a set of channels—that are isolated from the feed/retentate fluid by gaskets—and acts as a header leading to the permeate outlet from the module.

8) are a fully integrated vessel with membranes (that is, the membrane elements are not replaceable). Maximum operating pressures up to 1 MPa are typically available.

Figure 9 presents a schematic of cross-flow pressure-driven membrane filtration processes for liquids. The crossflow configuration helps control concentration polarization and cake buildup. This means that higher permeation rates can be maintained over extended periods of time versus what would be the case in dead-end filtration. Higher permeation rates are especially useful when continuous operation is desired, such as when there is the need to process large volumes of material and minimize adsorption of solutes on the membrane material. These modules are also amenable to cleaning by a number of different protocols. Also backpulsing (providing a short-duration backward flow of clean fluid from the permeate side to the feed side of the membrane) can be implemented during continuous operation to periodically release cake buildup and cause an increase in permeation rates.

Hollow fiber modules are especially used for gas hydration or dehydration, as well as gas dissolution in fluids. They are also available for microfiltration (MF), ultrafiltration (UF), and dialysis type applications. Some modules have been designed with liquid-liquid extraction applications especially in mind.

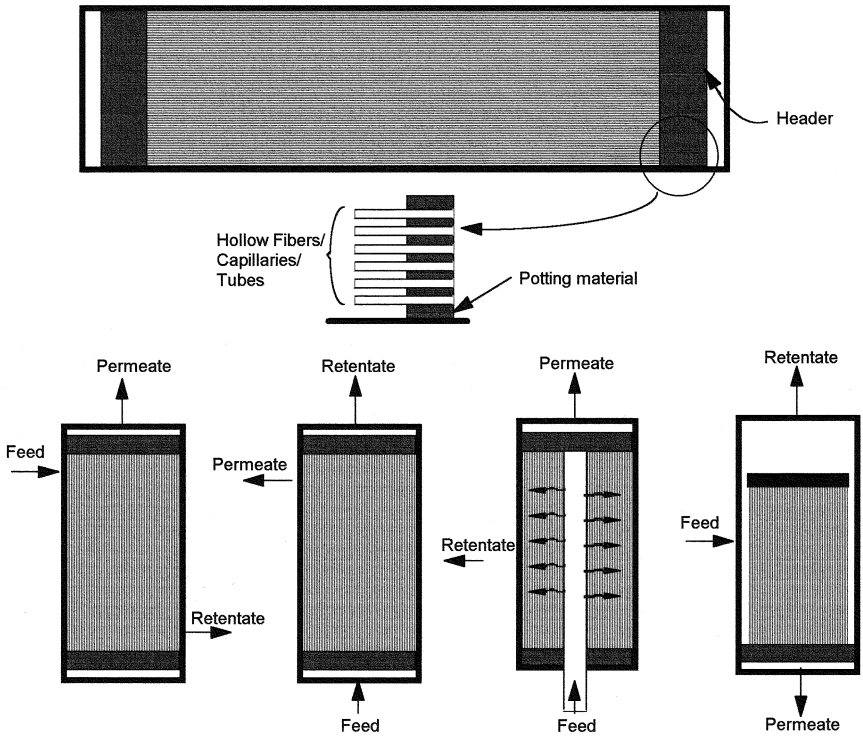

Figure 8. Schematic of a hollow fiber (or tubular) membrane module and several possible flow configurations that may be used. It is also possible to have an additional inlet port used to provide an initial "sweep" or diluent for the permeate stream. This would be the case in a membrane air dryer where an internal recycle loop directs some of the dehumidified air to permeate side of the membrane near to where the incoming air feed enters.

MEMBRANE AND FILTER TRANSPORT PROPERTIES

Solvent and Solute Flux

The flow through a *clean* membrane or filter is controlled by its specific hydraulic permeability, the thickness of the separating layer, the area of membrane presented to the feed, the TMP, and the viscosity of the fluid passing through it. A membrane or filter does not stay clean very long, so a more generalized viewpoint includes the flow restrictions due to concentration polarization, cake buildup, surface fouling, and pore plugging. Therefore, in practice, if the TMP is kept constant, the solvent flow (flux) through the membrane or filter will change with time.

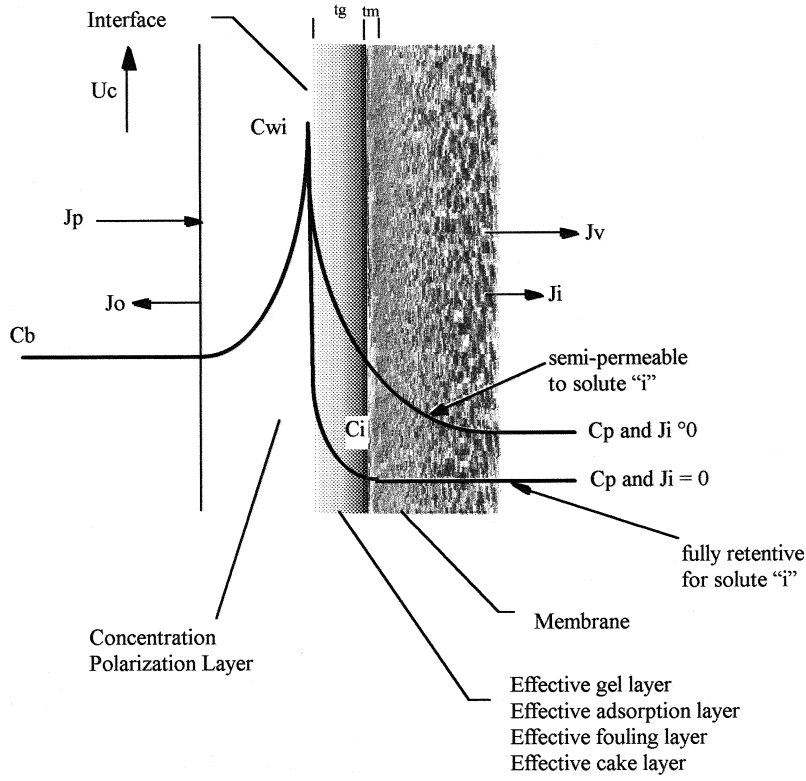

Figure 9. General model of a differential "slice" of a pressure-driven liquid filtration process. In crossflow the bulk fluid velocity $U_c > 0$ and in dead-end filtration (without stirring) $U_c = 0$.

The basic observed flow quantity is the flux. Simplified general expressions for the solvent and solute flux are given by equations 1 & 2 (refer to Fig. 9). Note that these expressions contain several quantities that can (and will) vary with both time and position along a membrane or filter's surface. Prediction of transport through semipermeable membranes requires trial-and-error calculation because the permeation of both solvents and solutes depend on each other. In addition, a model for the mass transfer boundary layer is required to predict the concentration at the membrane interface based on the bulk concentration and the actual hydrodynamic conditions in the membrane device. Manufacturers can usually provide guidance in this regard.

For dialysis-type applications convective flow of both solvent and solute will be negligible. Solvent and solute(s) permeability coefficients will essentially

be based on their respective solubility and diffusivity through the membrane. The mass transfer driving force for flux will be based on the activity (concentration) of the components in the feed and permeate. On the other hand in microfiltration (both depth and surface) the solvent and solute flux will pretty much be controlled by convective transport. The TMP will not be significantly affected by osmotic pressure gradients. The changes in hydraulic resistance due to fouling (external and internal) and surface layer accumulation will be the main phenomenon controlling flux.

Solvent flux is given by

$$J_v = \frac{\Delta P - \Delta\pi}{\left[\frac{t_m}{P'_v} + \frac{t_g}{P'_g}\right]\eta}, \tag{1}$$

and solute flux by

$$J_i = J_v(1 - \sigma_i)C_{wi} - \frac{J_v(1 - \sigma_i)(C_{pi} - C_{wi})}{\exp(J_v(1 - \sigma_i)/P_{mi}) - 1}. \tag{2}$$

Membrane and filtration parameters:

- U_c crossflow velocity, m/s. This quantity is 0 in dead end filtration.
- J_p the flux of solute toward the membrane interface, mol m^{-2} s^{-1}. This quantity is a natural result of the permeation process.
- J_o the flux of solute back into the bulk feed, mol m^{-2} s^{-1}. This quantity results from back diffusion and convective processes at the feed-membrane interface.
- C_b bulk concentration of solute in the feed solution, mol/m^3.
- C_{wi} concentration of solute at the interface between the feed and the membrane's surface including any surface layer (gel/cake/etc.), mol/m^3. This quantity is the maximum solute concentration in the concentration polarization layer. *The concentration polarization layer* is the mass transfer boundary layer in which the concentration of solute increases relative to the bulk feed solution. This layer occurs because $J_p > J_o + J_i$.
- C_i concentration of solute at the membrane's surface, mol/m^3. This quantity may be different than C_{wi} because of the sieving properties of the layer(s) sitting on the membrane's surface.
- C_{pi} concentration of solute I (i.e., a protein) in the permeate, mol/m^3. This quantity is zero for those solutes completely rejected by the membrane or filter.
- J_i the flux of solute i into the permeate, mol m^{-2} s^{-1}. This quantity is zero for those solutes completely rejected by the membrane or filter.
- J_v the water (solvent) flux, m^3 m^{-2} s^{-1}. This quantity is the measured permeation rate, including solutes, divided by the available filtration area.

P'_v specific water conductance of a clean membrane, $m^3\ m^{-1}$, where t_m/P'_v is the compressed membrane or filter's hydraulic permeability based on Darcy's relationship.

t_m thickness of membrane's permselective layer, m. This will be the entire membrane thickness if it is not an asymmetric structure.

P'_g specific water conductance of the surface layer, $m^3\ m^{-1}$, where t_g/P'_g is usually determined experimentally as a specific overall resistance.

t_g thickness of the surface layer, m (gel/cake/adsorption/fouling).??The surface layer may be the result of only one type of phenomenon for simple feeds. With complex feeds it is likely that several types of layers result. Pore plugging may also be included in this empirical approach.

ΔP applied, transmembrane, mechanical pressure (at a specific point), kPa.

Δp actual osmotic pressure gradient based on C_w and C_p (at a specific point), kPa. This quantity will not be very large for microfiltration processes.

η solution viscosity, kPa s. This quantity can vary through the surface layer of the membrane due to the effect of increasing solute concentration (due to rejection by the membrane) on viscosity. It is also a function of temperature.

P_{mi} the specific solute's permeability coefficient, $m\ s^{-1}$. This is a transport parameter that relates to the rejection of a solute in *diffusive transport*. It is measured when $J_v = 0$.

σ_i the solute reflection coefficient, dimensionless. This is a transport parameter that relates to the rejection of a solute in *convective transport*. When $\sigma_i = 1$ there is no solute permeation.

Solute Rejection

Solute rejection (or the permselectivity) of a membrane or filter is defined for each main solute or family of solutes. For example, monovalent versus divalent ion transport, molecular mass discrimination between small organic molecules, oligomers, and macromolecules, and sieving of particulates, colloids, and cells. The most commonly used figures-of-merit to define performance of a membrane or filtration operation are defined as follows:

- R (observed solute rejection) = 1- C_p/C_b - dimensionless. This quantity is what is measured by sampling the bulk feed (and reject) and permeate phases.
- R° (intrinsic solute rejection) = 1- C_p/C_w - dimensionless. This quantity takes into account the real solute concentration at the membrane interface.

- S_{50} (sieving coefficient) = C_p/C_b - dimensionless. This quantity is measured in batch filtration after 50% of the feed has been filtered. It is related to the observed rejection.
- LRV (log reduction value) = $-\log_{10}(S_{50})$. Thus the higher the LRV the greater the rejection of the challenge particles by the membrane or filter.

These quantities are actually measured in a particular application and would not be readily available as a specification.

To help guide the choice of a membrane for a particular purpose, manufacturers typically provide a pore size (diameter) rating (filters and microfiltration) or a MWCO (ultrafiltration). Both of these ratings should only be taken as a very coarse characterization of the filter or membrane. No standard techniques have been adopted for the measurement of these parameters so several approaches are widely used for each.

Pore Characteristics

A membrane and filter allows the permeation of solution based on the sizes and number of pores that allow the solution to enter and pass through to the other side. Membranes and filters can have both open pores (communication with both external surfaces) and closed pores (communication with only one or no surface)—but hopefully few of the latter. Those solutes that cannot enter the pores will be rejected. The general terminology of pores (and the types of filtration processes) is given in Table IV.

Meso-and macropores are those commonly associated with the pressure-driven liquid filtration process encountered in the general laboratory environment. Dialysis and gas dehumidification using membranes will typically use materials having ultramicropores and smaller, though at this length scale the term "connected free volume" is also used instead of pore.

A specific membrane or filter will have a pore size distribution, a surface porosity, and a pore shape. The pore size distribution and surface porosity will of-

Table IV. General Terminology of Pores

Macropore	width $>$ 50 nm	UF, MF, and filtration
Mesopore	2 nm $<$ width $<$ 50 nm	UF, NF
Micropore	width $<$ 2 nm	NF
Supermicropore	0.7 nm $<$ width $<$ 2 nm	RO, NF
Ultramicropore	width $<$ 0.7 nm	RO, GS, dialysis
Ultrapore	width $<$ 0.35 nm	RO, GS, dialysis

(UF - ultrafiltration, MF - microfiltration, NF - nanofiltration, RO - reverse osmosis, GS - gas and vapor separation)

ten depend on each other for a specific material and type of membrane. This is because of the physics of forming the pores in a thin film. Different materials and formation processes will be bounded by different constraints (for example, the shape and size of polymer nodules in the initial casting solution or the electrochemical cell design for anodically-deposited alumina). Thus, a variety of membranes from different manufacturers—for example, rated at 10 kDa MWCO—can have very different water permeabilities. Additionally, variations in the pore size distribution, pore shape, and internal tortuosity can again result in differences in both permeability and solute rejection characteristics for membranes rated with the same nominal pore size or MWCO. Also, the chemical nature of the membrane material (i.e., ionizable groups) will greatly influence solute rejection depending on the solutes evaluated.

Measurement of Pore Size and Solute Rejection Properties

While seeming like a "dog chasing its own tail", solute rejection measurements are also sometimes used as a surrogate for a geometric measurement of the pore size and distribution. Therefore, we include discussion of those techniques in this section. Overall there are three basic characterization approaches: 1) observation or visualization methods (including x-ray and neutron spectroscopies), 2) flow and intrusion of fluids coupled with fitting a model, and 3) transport or phenomenological measurements. The following are brief summaries of several commonly used methods.

Visualization Methods

Microscopic approaches typically include: optical (resolution $\sim$ 0.5 μm), transmission electron microscopy (resolution to 1 nm), scanning electron microscopy (resolution $\sim$ 2–6 nm). The electron microscopies require sample preparation that can introduce uncertainties in the accuracy of representation. Microscopic techniques also visualize only a small fraction of the surface. Scanning probe microscopies can resolve to the same level as electron microscopies but don't require special sample treatment and can scan larger areas of the membrane surface. All the visualization techniques can provide a measure of the overall size distribution, shape, and number density (porosity) for surface pores.

Hydraulic Permeability

The flow rate through the membrane or filter is measured at a single TMP. A pore length and tortuosity, and an overall membrane porosity must be assumed

or measured by some other means. All the flow is assumed to go through a single size pore.

Bubble Pressure or Point (also Gas-Liquid Porosimetry)

The membrane or filter is filled with a wetting liquid and a gas pressure is applied and increased. The differential pressure necessary for the bubble of gas to displace the liquid filling the pore is used to calculate that pore's diameter using the assumption of circular cylindrical pores. The surface tension (for the liquid/gas) and the contact angle (liquid/gas/membrane material) are needed. Bubbles (representing gas penetration) can be determined visually or by electronic flow sensors. As the pressure is increased smaller diameter pores are emptied. By measuring the total volume of gas (the displacing fluid), as a function of differential pressure, a pore size distribution can be obtained. This method is subject to many measurement uncertainties and will often underpredict the size of the largest pore. Improved equipment designs and the use of empirical correction factors can reduce the measurement uncertainty. It is typically used for materials with pores >0.15 μm due to the TMP required to displace liquid from smaller pores.

Liquid Displacement (also Liquid-Liquid Porosimetry)

This follows the same principles as the bubble pressure technique but uses a second liquid, that is immiscible in the liquid filling the membrane's pores, instead of a gas. Both liquids are chosen to have low surface tensions and therefore lower TMP can be used and smaller pores (~ 0.002 μm) can be measured without unreasonably high mechanical pressures. The uncertainty in the pore size results can be high due to non-equilibrium wetting effects, membrane swelling, and experimental measurement uncertainties.

Gas-Liquid Diffusion

The membrane's or filter's pores are fully wetted by a liquid and the diffusion of a gas through those pores is measured. Using the known solubility and diffusivity of the gas in the liquid an average pore thickness and tortuosity are calculated. The pressure of the gas is increased to vent pores of increasing pore diameter. The convective gas flow is measured and a pore size distribution is determined. This technique is predominantly used to detect defects in modules.

Permporometry

The membrane or filter is clamped between two flowing gas streams, The permeate side of the membrane is swept by a single inert gas (e.g., N_2). The feed side of the membrane is swept by a mixture of the inert gas, a condensible vapor, and a probe gas that is quantitatively measurable in trace levels (e.g. O_2). The partial pressure of the condensible vapor is raised and lowered to close or open pores of different size (typically 0.001–0.025 μm). As pores are opened the volume of O_2 that diffuses into the permeate-side stream will increase in proportion to the number and size of open pores. The uncertainty in the pore size results can be due to membrane swelling, insufficiency of a cylindrical pore model, and experimental measurement uncertainties.

Gas Adsorption-Desorption (also Called Brunauer, Emmett, and Teller, or BET Method)

The pressure of a condensible gas is increased to provide monolayer, then multilayer sorption on internal surface area of pores, until full condensation occurs. Then the procedure is reversed. The hysteresis between filling and emptying the pores provides a measure of the pore volume distribution. The internal surface area at monolayer coverage is then used to calculate a pore diameter distribution. This method requires dry membranes and low temperatures that may introduce material artifacts.

Polydisperse Solute Rejection (also MWCO)

This method is based on steric or size-based rejection of solutes by a membrane pore. Typically, a mixture of water soluble molecules and/or macromolecules is made and presented as the feed to the membrane. For dialysis, reverse osmosis, or nanofiltration membranes the mixture will typically contain mono-and divalent salts, urea, sucrose, and alcohols. For ultrafiltration and small-pore microfiltration membranes the macromolecule solution can be a mixture of proteins or a polydisperse solution of a single hydrophilic polymer, such as dextrans, polyethylene glycols, or ficolls. The molecular mass distribution is measured on the starting feed material (usually by size exclusion chromatography, SEC) and the permeate. The result is a curve of % rejection against molecular mass. The membrane is usually rated by the mass at which 90% of the solute is rejected.

Among the main sources of uncertainty are the assumptions of solute rejection based on size alone and that the solute's shape (and therefore dimensions) re-

mains invariant. The partitioning of macromolecules into pores is based on size, shape, energetic interactions (i.e., electrostatic) between solutes and the membrane material, and the concentration at the pore mouth. The concentration will depend on the conditions under which the filtration measurement was performed (concentration polarization is a factor). The solutes' size, shape, and energetic interactions will also depend on the overall solution conditions (pH, ionic strength, temperature). Also specific and non specific adsorption of the solutes to the membrane surface can occur causing an overestimate of percent rejection. Another source of measurement uncertainty is the calibration of the SEC column. Therefore ratings of MWCO should not be taken as a geometric absolute. The results obtained in such measurements are a "snapshot" of the membrane's transport characteristics under a specific set of measurement conditions.

Particle Retention

Filters and microfiltration membranes for both liquid and gas filtration applications are often characterized by particle (e.g. latex) retention (aka rejection) measurements. Particle rejection is typically expressed in terms of the LRV (previously defined in the section on **Solute Rejection**). The feed stream is usually referred to as a "challenge" and the challenge level may be "dilute" 10^8–10^{10} particles/L or "concentrated" $10^{13}-10^{15}$ particles/L. Both monodisperse and polydisperse particles are used. The instrumentation is typically laser particle sensing and counting with automated data collection and analysis. Particle retention can occur by both depth (throughout the thickness of the filter) and surface capture mechanisms. Measurements of particle retention are not without ambiguity. The relationship between the actual geometric dimensions of the membrane or filter and the size of the particle being retained is most tenuous if the filtration occurs throughout the filter's depth. This is due to the variety of depth filtration capture mechanisms (e.g., inertial impaction, interception, diffusion, electrostatic attraction) that facilitate the retention of particles smaller than the openings in the filter's structure. These considerations are particularly noteworthy in gas filtration.

Since many mechanisms contribute to the particle rejection, filter performance can change with both time, loading, and particle size distribution. For instance, under some circumstances "breakthrough" (that is, loss of rejection after a period of time) occurs. It can be due to blockage of smaller voids thus causing more particles to challenge the larger ones. It is also true that the majority of convective flow through a filter is carried by the largest pores. Such a situation will also lead to those larger pores becoming partially or fully blocked by the captured particles. Thus the pore size distribution will apparently change with the extent of filtration. Thus, overall surface cake buildup, filter surface fouling, particle ag-

gregation, and particle bleedthrough can lead to changes in apparent filter retention and permeability.

Microbial Retention

Microbial organisms are often used as the particle challenge to filters and microfiltration membranes. This is especially the case for those membranes and devices focused toward medical and pharmaceutical applications. LRV is again the measure of the particle rejection by the filter. Microbes are considered a mondisperse particle size challenge to the microfilters. The nominal dimensions of the challenge organisms are used to develop the rating size of the filter. *Pseudomonus diminuta* (*P. diminuta*), 0.3 μm in diameter with an aspect ratio of 1.5 to 1, is widely recognized as a standard bacterium for testing sterilizing filter integrity. Thus we have the popular microfilter pore size ratings of 0.22 and 0.45 μm.

The bacterial challenge test for "sterilizing microfilters" is 1×10^7 organisms/cm^2, with no detectable organisms in the permeate. Testing of 0.22 and 0.45 μm filters at ~0.4 MPa have demonstrated complete retention of *P. diminuta* with 0.22 μm filters and an LRV of 9 with 0.45 μm ones. Organisms with different dimensions are also used to characterize the retention (nominal pore rating) of microfilters. Use of organisms to define pore size ratings can have a variety of causes for uncertainty. These include ineffective colloidal stabilization leading to aggregation and shape (dimension) change under the test conditions.

Measurement and Interpretation of Surface Properties

Materials are commonly referred to as hydrophilic (water wetting) or hydrophobic (not water wetting). This is a qualitative description of the contact angle at the air-water-solid interface. A contact angle (measured from the solid through the liquid to the air interface) of 0° means complete wetting, and an angle of 90° or greater indicates non wetting. Note that different contact angles will exist for solvents other than water. Thus, there are also the descriptors, lipophilic and lipophobic, referring to wetting by "oils." The contact angle measured on membrane and filter surfaces will often not match data obtained using very flat surfaces of the same nominal material. This is because (1) the surface texture (roughness) will lead to an "apparent" contact angle when viewed macroscopically, which integrates how the liquid contacts all the microscopic geometric surfaces, and (2) the wetting liquid can become absorbed into the membranes.

The fundamental characteristic of a material surface is its surface energy. High energy surfaces are more hydrophilic and contain polar and/or ionizable

groups. Low energy surfaces are more hydrophobic and are usually olefins, fluorocarbons, or minimally substituted aromatics. Some membranes and filters will be made from polymers with low surface energy (such as polypropylene) but may be treated in some fashion to increase the hydrophilicity of the surface. Treatments include surfactant coatings and grafting of functional groups.

Streaming potential measurements provide an indication of the surface charge. Surface charge will result from ionizable groups on the membrane's or filter's surface or ions (and ionizable species) preferentially adsorbed from the solution. This measurement is not routinely performed on membranes and filters because calibration standards and standard protocols do not exist. Relative results obtained on different materials are used to imply a qualitative difference in their surface properties.

Solute-membrane affinity is a very complex subject that is the focus of much research and development. Tailoring the surface chemistry of membranes or filters will often have as an objective to decrease the irreversible adsorption of solutes from the feed. Such a decrease will help control fouling. But the surface chemistry will also affect the partitioning of solutes into the membrane pores and the percent recovery of solutes that should completely pass through the membrane or filter. Thus, it is important to understand that often only the nominal material composition is provided by manufacturers for their membrane and filtration products. There will be proprietary formulations, including both the bulk material and any post membrane-formation treatment, that exist to further differentiate membranes that are nominally the same.

The surface texture (or roughness) of membranes and filters can be quite variable. The manner in which they are made, and from what starting materials, will to a great degree control the surface texture. The role of surface texture in the various phenomena associated with filtration processes is an active research topic.

SUGGESTED READING LIST

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