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A General Diagram for Estimating Pore Size of Ultrafiltration and Reverse Osmosis Membranes

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NOTE

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Abstract

A slit sieve model has been used to develop a general correlation between the average pore size of the upstream surface of a membrane and the molecular weight of the solute which it retains by better than 80%. The pore size is determined by means of the correlation using the high retention data from an ultrafiltration (UF) or a reverse osmosis (RO) experiment. The pore population density can also be calculated from the flux data via appropriate equations.

INTRODUCTION

Membranes are being increasingly used as a valuable separation tool in laboratory procedures as well as in industrial processes. Flourishing interests in the development and application of new membranes make it imperative to have simple and inexpensive calibration procedures accessible to membrane fabricators, investigators, and users. Methods of characterizing the pore size of RO and UF membranes include measurements of liquid (water) and gas flow, bubble point determination, electron microscopy, and molecular weight cut-off characterization. Most of these techniques, except the last one, involve relatively elaborate, time-consuming procedures. Because of its simplicity, molecular weight cut-off characterization is being used by most manufacturers in order to characterize their various membranes.

Molecular weight cut-off characterization simply involves finding an inert solute (preferably rigid and monodisperse) which has the lowest molecular weight that is more than 80% but definitely less than 100% retained by the membrane in a steady-state RO or UF experiment. Here precent solute retention, SR%, is defined as $(1 - C_p/C_f)100$, where C_p and C_f are the solute concentrations in the permeate and the feed solutions, respectively, in a well-stirred RO or UF experiment.

This method applies to homogeneous as well as heterogeneous membranes, and the molecular weight of the solute retained depends only on the structure of the upstream surface layer of the membrane (*1*). Such characterizations, however, do not define the pore dimensions involved. Therefore, a correlation between the molecular weight cut-off and the membrane pore size has been established so pore size can be determined.

PROPOSED METHOD

Viewing the UF and RO membranes as sieves, in order to develop the relationship between the molecular weight cut-off and the membrane pore size, it is first necessary to find a way of translating the solute molecular weight into a corresponding molecular size and from the latter estimate the pore size via a valid mathematical model.

Figure 1 represents the relation found between the molecular weight of the solutes commonly used in molecular weight cut-off determinations and their molecular radii in aqueous solutions. As for the relationship between the solute radius $\bar{a}$, solute retention SR%, and the average pore size $\bar{R}$, a variety of pore models may be used. Since at steady state, retention is solely controlled by the upstream surface structure (porosity) of the membrane, the sieving effects at the pore entrance are only to be considered (i.e., frictional effects within pores play no role in separation) (*5*). Three entrance sieve models have been developed in the past (*6–8*). These include: (a) circular pore and plug flow regime, (b) circular pore/parabolic flow regime, and (c) slit pores/plug flow regime. A plot of SR% vs $\bar{a}/\bar{R}$ for these three models shows that the three models converge at high values of $\bar{a}/\bar{R}$ which correspond to SR% values of greater than ~80% (*9*). This indicates that at high retentions the three models become equivalent and the slit model, which is mathematically simpler, i.e.,

$$\mathrm{SR\%} = 100(\bar{a}/\bar{R}) \tag{1}$$

may be used to determine the average pore size, where $\bar{R}$ refers to half width of the slit or pore radius. Thus, by measuring the solute retention of the membrane against a solute of known moleular weight (known $\bar{a}$ via Fig. 1), one can compute $\bar{R}$ from Eq. (1). The computed $\bar{R}$ will be more dependable particularly if SR% > 80%.

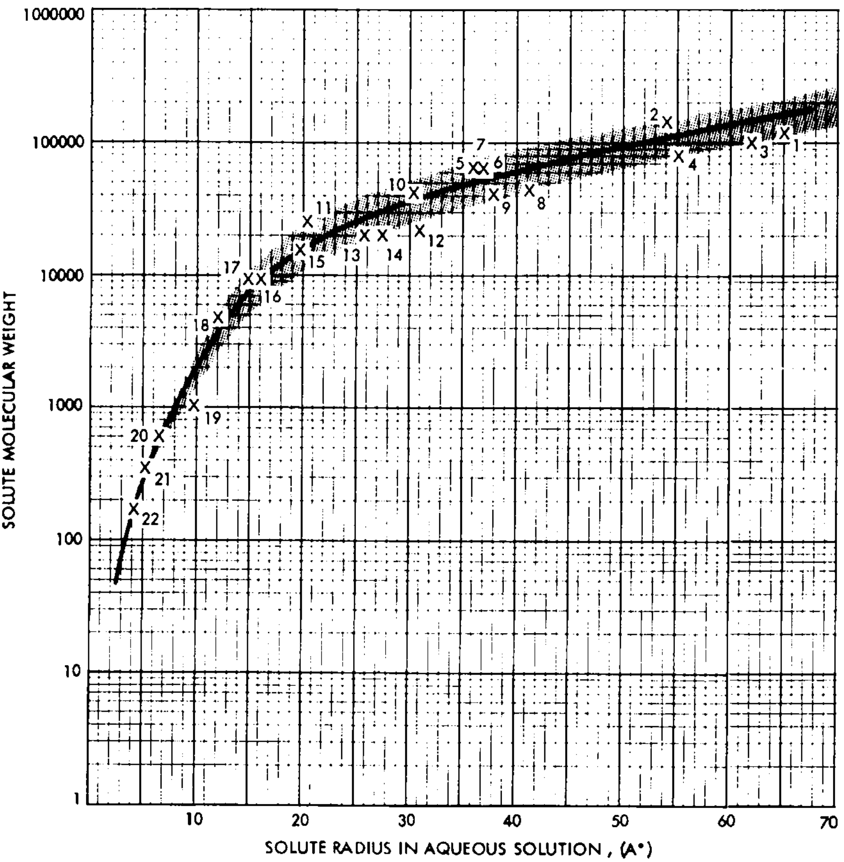

FIG. 1. Relation between molecular weight of solutes commonly used in MW cut-off determination and their average radii, $\bar{a}$, in aqueous solutions. The solid line represents the median correlation. The numbers on the diagram are represented as follows: (1) dextran, (2) aldolase, (3) dextran, (4) dextran, (5) human serum albumin, (6) bovine serum albumin, (7) albumin, (8) polyethylene glycol, (9) dextran, (10) ovalbumin, (11) α-chymotrypsinogen A, (12) polyethylene glycol, (13) dextran, (14) polyethylene glycol, (15) polyethylene glycol, (16) dextran, (17) polyvinylpyrrolidone, (18) inulin, (19) inulin, (20) raffinose, (21) sucrose, (22) glucose. Molecular radii of proteins, inulins, raffinose, sucrose and glucose were Stoke's radii obtained from the literature (*2*). For dextrans an average value between the radius of gyration of a real chain (*3*) a_r, and a geometric chain (*3*), a_g, i.e., $a = (a_r + a_g)/2$, was chosen. Here $a_r = (1.4n^{1.18}/6)^{1/2}l = 0.096M^{0.59}$ and $a_g = (n/6)^{1/2}l = 0.128M^{0.5}$, where M = molecular weight of dextran polymer (assumed a linear chain), n = number of glucose monomer units on the polymer chain, and l = 4Å = size of the glucose monomer unit. The calculated radii are in close agreement with the experimentally measured values reported in the literature (*4*). For polyethylene glycols and polyvinylpyrrolidone, their geometric radii of gyration were used. It might be added that the closest exponential fit for the above data is $\bar{a} = 0.5279M^{0.3915}$, with correlation coefficient r^2 of 0.94.

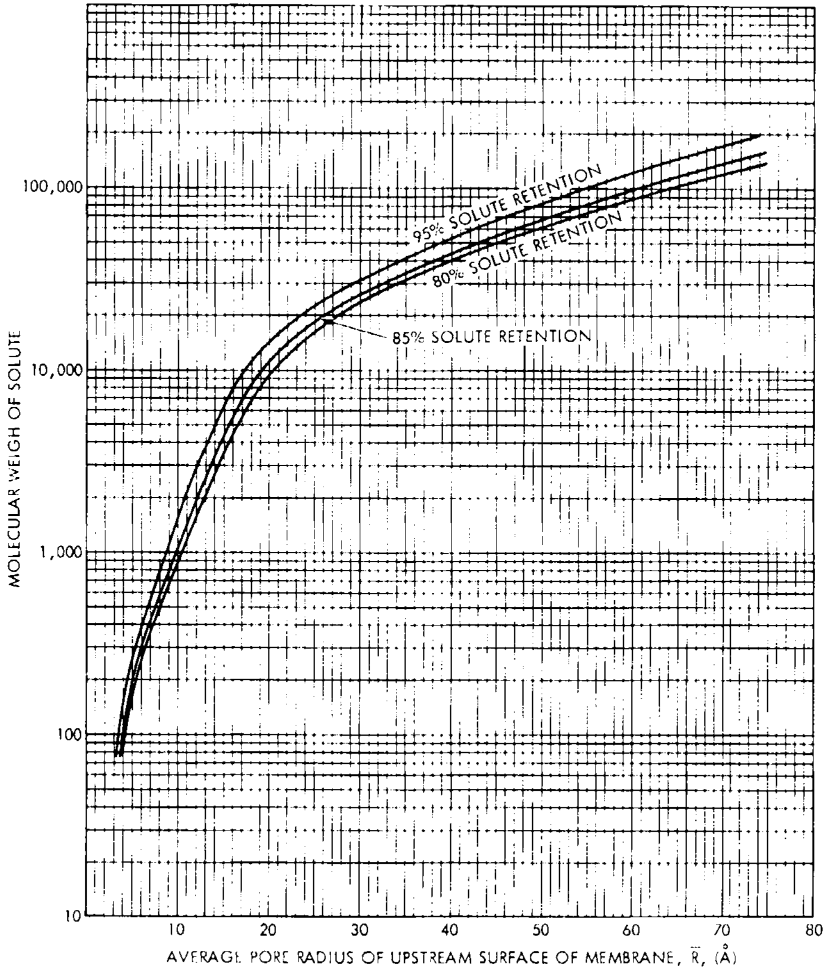

FIG. 2. Relation between solute molecular weight and the average pore radius of the upstream surface of the membrane at 80, 85, and 95% solute retention levels. This figure is derived from the combination of Fig. 1 and Eq. (1).

Through the combination of Fig. 1 and Eq. (1), a general correlation between the membrane pore size and the solute molecular weight at SR% = 80, 85, and 95% has been generated in Fig. 2. Additional curves corresponding to other values of SR% between 80–100 may be generated likewise, but for the sake of clarity they are not included. With the aid of this diagram, one can directly read off the average pore size of the membrane once an inert solute has been found whose SR% > 80%, i.e., once its molecular weight cut-off has been determined. For example, if a UF membrane exhibits a solute retention of 95% against 70,000 molecular weight dextran (at steady state in a well-stirred system), its average pore radius (upstream) is read as 46 Å.

To verify the validity of Fig. 2, the available data (molecular weight cut-off) on commercial membranes were used to read off their corresponding average pore radii. The results are shown in Table 1 where they are compared with the manufacturer's reported pore sizes as well as those reported in the literature based on electron microscope examination (*10*) and flow measurement techniques (*11*). It is seen that the estimated pore sizes from Fig. 2 are in surprisingly good agreement with others considering the assumptions made in the derivation of the pore model such as monodisperse rigid solute molecule and monodisperse pores as well as manufacturing variations and handling complications.

This result lends support to a similar conclusion reached by others who report that the slit pore model explains the electro-osmotic data better than circular pore models (*8*).

TABLE 1

A Comparison of the Average Pore Radii, $\bar{R}$, Obtained from Fig. 2 with Those of the Literature and Manufacturer

Amicon Membranes

Identification code	UM05	UM2	YM5	UM10	PM10	XM50	XM100
Manufacturer's reported SR%	90	80	90	90	65	80–100	80–100
At given MW	594	594	10,000	10,000	10,000	50,000	100,000
$\bar{R}$, by our method (Å)	9.3	12.7	16.3	18.2	21.8	37–46	53–63
$\bar{R}$, from literature (Å)	—	—	—	7-15 (*10*)	10–20 (*10*)	30–73 (*11*)	68–76 (*11*)
$\bar{R}$, from manufacturer (Å)	10.5	12	—	15	19	33	55

Millipore Membranes[a]

Identification code	PSAC	PTGC	PSED	PTHK
Manufacturer's reported SR%	85	85	98	93
At given MW	1000	10,000	25,000	100,000
$\bar{R}$, by our method (Å)	14.1	22.1	31.7	62.7

[a] No literature data were found for these membranes.

Once the average pore size is determined from the SR% measurement and Fig. 2, the following equation, which describes flow through a circular orifice (and therefore is applicable only to asymmetric skin type membranes), may be used to estimate surface porosity, ε, total pore area per unit surface area (*12*)

$$\varepsilon = 3\Pi \eta J / \bar{R} \Delta P \tag{2}$$

where η = viscosity of the permeate (g/cm · s), J = pure solvent flux (cm/s), and ΔP = the applied pressure (dyn/cm^2). Knowing ε and $\bar{R}$ (in cm), one can then calculate pore density from

$$n = \varepsilon / \pi \bar{R}^2 \qquad \text{pores/cm}^2 \tag{3}$$

If the membrane is homogeneous throughout its thickness, instead of Eq. (2) one must use Poisseuille's law,

$$\varepsilon = 8 \eta l J / \bar{R}^2 \Delta P \tag{4}$$

where l = membrane thickness (cm).

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