

Pore Size of Microporous Polymer Membranes

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Synopsis

Pore sizes of microporous polymer membranes were determined by the calculation based on the gas permeability of porous media. The gas permeability coefficient K (given by $J = K \Delta p/l$, where J is the steady-state gas flux, Δp is the pressure difference, and l = the thickness of a membrane) for porous membrane can be given generally by

$$K = K_0 + \frac{B_0}{\eta} \Delta \bar{p}$$

where K_0 is the Knudsen permeability coefficient, η is the viscosity of the permeant gas, B_0 is the geometric factor of a membrane, and $\Delta \bar{p}$ is the mean pressure of the gas on both sides of a membrane. From gas permeability measurements which yield the pressure dependence of gas permeability coefficient (expressed as above equation), the mean pore size of the porous membrane can be estimated as

$$m = \left(\frac{B_0}{K_0} \right) \left(\frac{16}{3} \right) \left(\frac{2RT}{\pi} \right)^{1/2} M^{-1/2}$$

where M is the molecular weight of the permeant gas. The validity of this method was examined with various Millipore filters of which nominal pore sizes are known. It was confirmed that the method provided a simple and reliable means of estimating mean pore size of microporous membranes. The method was applied to investigate the influence of factors involved in preparation of microporous polysulfone membranes by coagulation procedure. It was found that the mean pore size of porous polysulfone membrane increases with (1) increasing casting thickness, (2) increasing temperature of coagulation bath, and (3) decreasing concentration of polymer in casting solution (DMF as solvent). Water flux and water flux decline due to compaction are also examined as a function of pore size, porosity, and the thickness of membranes.

INTRODUCTION

Porous polymer membranes have drawn considerable attention in practical use in recent years. Depending on their pore size, porous polymer membranes can be used in a variety of fields such as removal of particulates from air, filtration of colloidal suspension, aseptic wrapping of biomedical supplies, transfer surface through which gases are transferred into liquid(s), and support for ultrathin semipermeable membranes. The pore size of porous polymer membrane plays the most important role in the function of porous membranes in these applications.

Although several methods to estimate mean pore size of porous membranes are available, the methods generally involve some ambiguity such as (1) tortuosity factor and (2) the perturbation caused by the measurements; e.g., wetting by liquids or penetration of mercury under pressure to estimate porosity may alter the pore sizes of original membranes. Therefore, if it were possible to estimate pore size from gas permeation data alone, this would provide a simple means to characterize porous membranes (in dry state) without causing any alteration of structure by the measurement. Furthermore, it will provide perhaps the only accurate means to follow the changes that occur to the pores of porous membranes in some dry-state reactions such as spattering of metals onto a porous membrane and glow discharge deposition of polymer into a porous substrate under vacuum.

This study was undertaken in order to find a simple method of estimating and controlling the mean pore size of microporous membranes during membrane preparation and to use the method in investigating the process of glow discharge polymerization onto porous membrane which is used to prepare composite reverse osmosis membranes.

The term "microporous" may need some explanation, since the word "porous" has been often used without clear definition of pores. As far as the permeability of gases through polymers is concerned, there is a clear distinction between porous and nonporous membranes.¹ It should be noted that nonporous polymers are still permeable, and the concept of "pore" does not extend to the free volume or molecular level spaces where the passage of gases takes place in nonporous polymer membranes. In terms of pore size, the microporous membranes referred in this study may be considered as membranes of which pore size is of the order of 100 Å to 10,000 Å (1 μm).

The method was first examined using commercially available microporous membranes (Millipore filters) and was applied to investigate the factors that influence the porous size of porous polysulfone membranes.

EXPERIMENTAL

Gas Permeability Measurement

A porous membrane was placed in a Millipore high-pressure cell, and the assembled cell was connected to a stainless steel tank (1000 cu in. capacity) which has a pressure transducer. Schematic representation of the system is shown in Figure 1. After the tank was pressurized to a predetermined pressure, the ball valve between the tank and the permeability cell was opened and the decay of the pressure was recorded.

It was empirically found that the initial stage of pressure decay was not representative of steady flux. In order to avoid the initial transient stage of pressure decay, the tank was pressurized to a pressure approximately 50% higher than the pressure needed for the measurement, and gas was allowed to permeate through the test membrane before the recording of pressure was taken.

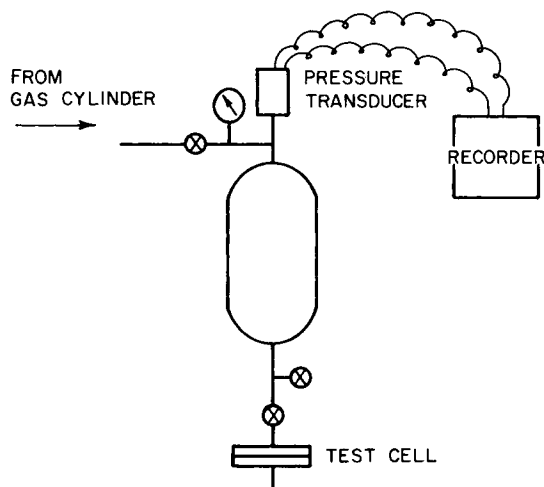


Fig. 1. Schematic representation of gas permeability measuring apparatus.

The slopes of the pressure decay curve were measured and recorded at various pressures on a linear strip-chart recorder and were used to plot against the mean pressure.

The identical system was used to measure the maximum pore size by bubble break-through measurement by simply connecting the downstream side of the test cell to a test tube containing water in which the connecting tube was inserted.

For the measurement of maximum pore size by bubble break-through measurement, a membrane was wetted by water or isobutyl alcohol before placing it on the test cell. The test cell with a wet membrane was connected to the tank system. The tank was pressurized slowly with the ball valve kept open, and the pressure at which the first gas flux in the downstream side of the cell was detected by the bubble detector was taken as the critical pressure p_c .

The maximum pore size was calculated by

$$m_x = \frac{2\gamma}{p_c}$$

where γ is the surface tension of the liquid that occupied the pore (water or isobutyl alcohol).

Preparation of Porous Polysulfone Membranes

The porous polysulfone films were cast from a 14% to 20% polymer in N,N-dimethylformamide (DMF) solution of polysulfone P-3500 provided by Union Carbide. Casting was performed at room temperature in a nitrogen atmosphere using a multiple-clearance applicator. Membranes were cast at designated wet thicknesses (4 to 10 mils) onto a Mylar film belt

moving a 100 cm/min into a temperature-controlled coagulation bath located 50 cm from the casting knife. Cast films were kept in the coagulation bath for approximately 10 min and were then transferred to deionized water (for 2 hr) and then hung in air to dry.

Water flux of porous polysulfone membranes was measured by connecting the Millipore test cell to a reverse osmosis test loop but using pure water at applied pressure of 500 psi. The steady-state water flux was obtained after 24 hr from the initial pressurization of the cell. The compaction factor was calculated as

$$\text{compaction factor} = \frac{\text{initial water flux}}{\text{steady-state water flux}}$$

The initial flux was taken 20 sec after the pressurization of a test cell. The water flux generally declined sharply in the beginning and leveled off after approximately 6 to 8 hr.

Calculation of Mean Pore Size m from Gas Permeability Data

Gas flux J through a membrane can be generally expressed by

$$J \equiv \frac{d(pv)}{dt} \frac{1}{\text{cm}^2} = K \frac{\Delta p}{l} \quad (1)$$

where K is the permeability coefficient (cm^2/sec) and Δp is the pressure difference (dyne/cm^2) across a membrane of thickness l (cm). (See Appendix for details of units of flux.)

Permeability coefficient K of porous media is shown^{2,3} to be expressed by

$$K = K_0 + \left(\frac{B_0}{\eta} \right) \Delta \bar{p} \quad (2)$$

where K_0 is the Knudsen permeability coefficient (cm^2/sec), η is the viscosity ($\text{dynes} \cdot \text{sec}/\text{cm}^2$) of the permeant gas, B_0 is the geometric factor of a membrane (cm^2), and $\Delta \bar{p}$ is the mean pressure. The mean pressure is given by the mean of pressures on both sides of a membrane; i.e., $(p_1 + p_2)/2$, whereas the differential pressure Δp is given by $(p_1 - p_2)$.

It has been shown that K_0 and B_0 can be generally expressed by the following two equations for practically all kinds of porous media²:

$$K_0 = \frac{4}{3} (\delta/k_1 q^2) \epsilon m \nu \quad (3)$$

and

$$B_0 = \epsilon m^2 / k q^2 \quad (4)$$

where $\delta/k_1 = 0.8$ for all membranes, $q =$ tortuosity factor, $\nu =$ average molecular velocity of a gas, $\epsilon =$ porosity, and $k = 2.5$ for all membranes.

The average molecular velocity of a gas of molecular weight M is given by

$$\nu = \left(\frac{8RT}{M} \right)^{1/2} \tag{5}$$

and can be considered as a constant for a gas at a given temperature.

The combination of eqs. (3), (4), and (5) leads to

$$m = \left(\frac{B_0}{K_0} \right) \left(\frac{16}{3} \right) \left(\frac{2RT}{\pi} \right)^{1/2} M^{-1/2}. \tag{6}$$

Equation (6) indicates that the mean pore size m can be calculated from the pressure dependence of gas permeability of porous membrane without further estimation of porosity ϵ and tortuosity factor q . The value of K_0 is obtained by extrapolation of permeability data to zero pressure, and B_0 is obtained from the slope of the extrapolation (linear line). An example of plot is shown in Figure 2. Equation (6) further indicates that the calculation of m does not depend on the nature of the measurement, since B_0/K_0 has the unit of time. In other words, any value of permeability in terms of pressure, volume, flow rate, etc., can be used directly in a plot against the mean pressure. The only necessary procedure is to obtain the intercept K_0 and the slope of the linear line of the plot. Therefore, insofar as obtaining the mean pore size is concerned, it is not necessary to obtain membrane area, membrane thickness, size of equipment, or some other calibration factors that are necessary to convert the measuring parameter (e.g., millivolts in recorder) to gas flux, as long as the proper units of pressure and viscosity are used.

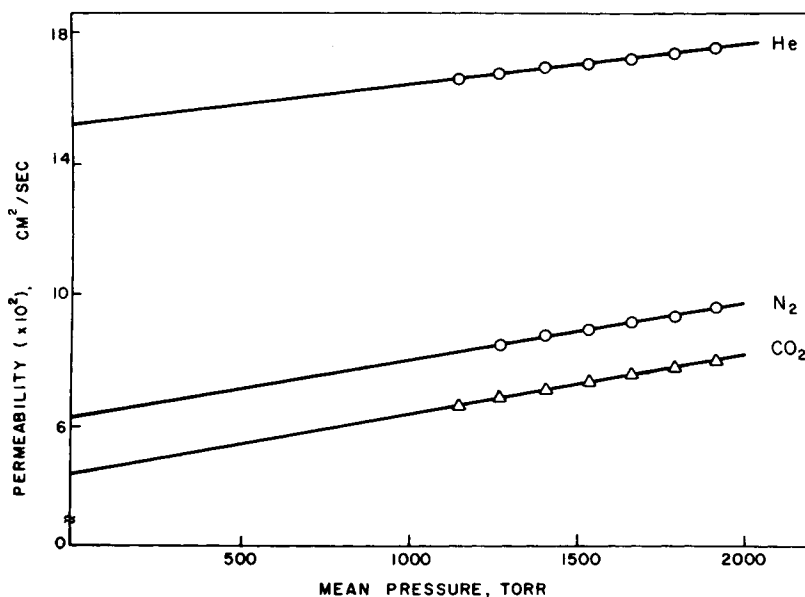


Fig. 2. Permeability coefficients vs. mean pressure. He, N₂, and CO₂, Millipore VM.

When a porous membrane is used with another porous support, the result obtained will depend on the pore size of the support. The effect of support can be analyzed by the situation of a porous-porous composite membrane.

The steady-state gas flux through a composite membrane that consists of two layers of porous membranes can be expressed using subscripts 1 and 2 to refer to membrane 1 and membrane 2, respectively, by the following sets of equations:

$$J = K_1 \frac{\Delta p_1}{l_1} = K_2 \frac{\Delta p_2}{l_2} = K \frac{\Delta p}{l} \quad (7)$$

$$\Delta p = \Delta p_1 + \Delta p_2 \quad (8)$$

$$l = l_1 + l_2 \quad (9)$$

Assuming that both layers are typical porous membranes i.e., K values can be expressed by eq. (2), the overall flow resistance of the composite membrane l/K can be given by

$$\frac{l}{K} = \frac{l_1}{K_{0,1} + (B_1/\eta)\Delta p_1} + \frac{l_2}{K_{0,2} + (B_2/\eta)\Delta p_2} \quad (10)$$

The overall Knudsen permeability of the composite membrane K_0 is obtained as $\Delta p \rightarrow 0$ and consequently $\Delta p_i \rightarrow 0$, so that

$$\frac{l}{K} = \frac{l_1}{K_{0,1}} + \frac{l_2}{K_{0,2}} \quad (11)$$

Designating $b_1 = B_1/\eta l_1$; $b_2 = B_2/\eta l_2$; $k_{01} = K_{01}/l_1$; and $k_{02} = K_{02}/l_2$, and solving eqs. (7) and (8) simultaneously in terms of Δp , we obtain

$$\Delta p_1 = \frac{-(k_{01} + 2b_2\Delta p) \pm ((k_{01} - k_{02})^2 + 4(k_{01} + b_1\Delta p)(k_{02} + b_2\Delta p))^{1/2}}{2(b_1 - b_2)} \quad (12)$$

where Δp should be positive and $b_1 - b_2 \neq 0$. On the other hand, substituting eq. (7) into eq. (2), we have

$$K/l = K_1 \frac{\Delta p_1}{\Delta p} \frac{1}{l_1} = k_{01} \frac{\Delta p_1}{\Delta p} + b_1 \frac{\Delta p_1^2}{\Delta p} \quad (13)$$

At relatively high pressure, the experimental results shown in Figure 3 indicate that K is a linear function of the (total) mean pressure; i.e., eq. (2) is also valid to the composite membrane. Equation (12) can be expressed by a Taylor series in terms of Δp

$$\Delta p_1 = \frac{k_{02}}{(k_{01} + k_{02})} \Delta p + \frac{(k_{01}^2 b_2 - k_{02}^2 b_1)}{(k_{01} + k_{02})^3} \Delta p^2 + \dots \quad (14)$$

Substituting eq. (14) into eq. (13) and comparing with eq. (2),

$$b = \frac{k_{01}^3 b_2 + k_{02}^3 b_1}{(k_{01} + k_{02})^3} \quad (15)$$

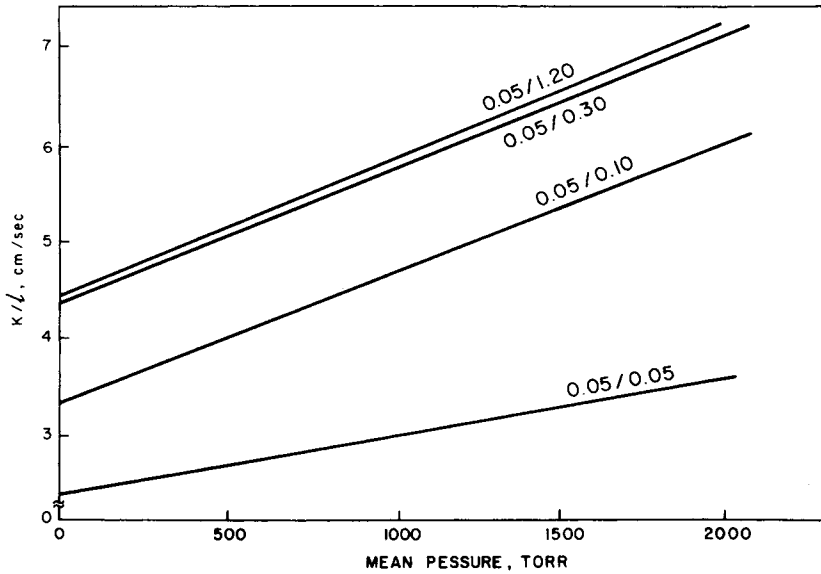


Fig. 3. Dependence of K/l of N_2 in composite membranes on mean pressure. K/l instead of K is used to obtain separation of lines. Nominal pore sizes of two layers are shown on each line.

Since $b_i = \alpha m_i k_{0i} = \alpha m_i K_{0i} / l_i$,

then

$$mk_0 = \frac{k_{01}k_{02}}{(k_{01} + k_{02})} \cdot \frac{k_{01}^2 m_2 + k_{02}^2 m_1}{(k_{01} + k_{02})^2}.$$

By virtue of eq. (11), therefore,

$$m = \frac{k_{01}^2}{(k_{01} + k_{02})^2} m_2 + \frac{k_{02}^2}{(k_{01} + k_{02})^2} m_1. \tag{16}$$

This result indicates that the average pore size of composite film is a summation of the contribution from each membrane. When the sub-structural pore size is relatively large, i.e., $k_{02} \gg k_{01}$, eq. (16) reduces to $m = m_1$. Evaluation by eq. (11) listed in Table II gave good agreement with experimental data. This method of evaluation can be applied to obtain the pore size of the coating layer where direct measurement of the permeabilities of the coating itself is impossible.

RESULTS AND DISCUSSION

Pore Size Determination

If the equations describing the permeability of porous membranes presented in the previous section are valid, the values of K_0 and slope of the plot (such as Figs. 1 and 2) should be dependent on the molecular weight

and viscosity of a gas used. However, the parameter B_0 and the mean pore size m of a membrane should be independent of the gas used as a permeant.

Calculation of mean pore size using various gases with the same membrane would provide proof of the method, although the physical meaning of mean pore size and its absolute value should be interpreted with caution. Data obtained with three different kinds of Millipore filters are summarized in Table I. Results indicate that the method provides consistent values regardless of the nature of gas.

TABLE I
Mean Pore Size Obtained with Different Gases

Membrane	Nominal pore size, μm	Calculated mean pore size, μm		
		He	N ₂	CO ₂
Millipore VS	0.025	0.030	0.034	0.032
Millipore VM	0.05	0.043	0.047	0.043
Millipore VC	0.10	0.10	0.11	0.11

The effect of porous support was examined using Millipore VM (nominal pore size 0.05 μm) with various porous supports. Results are summarized in Table II. Results shows that eqs. (13) and (16) are indeed valid for composite membranes and observed values of K_0 and m of composite membranes are in good agreement with corresponding calculated values. Results also indicate that if the pore size of support is much larger than the membrane, the observed mean pore size represents the value of the test membrane. However, if the pore size of porous support is comparable to the pore size of the test specimen, the observed pore size of the composite is in between the values of pore sizes of each layer. Even in the latter case, the pore size of the test membrane can be calculated according to eq. (16). This is an important aspect because many composite membranes can be

TABLE II
Mean Pore Size of Composite Membranes*

Pore size of support, μm	$K_0 \times 10^3$, cm^2/sec		Mean pore size of composite, μm	
	Observed	Calculated	Observed	Calculated
Without support	5.82	—	0.047	—
With filter paper	11.64	11.64	0.047	0.047
5.0 (nominal)	11.64	11.60	0.047	0.047
1.2 (nominal)	9.12	8.80	0.052	0.048
0.48	8.60	8.45	0.054	0.051
0.11	7.56	7.60	0.068	0.066
0.047	5.80	5.82	0.047	0.047

* Mean pore size was measured using N₂ as permeant gas. Millipore VM was used with various porous membranes as support.

tested only as a whole composite. Therefore, this method provides a useful means to estimating pore size of an ultrathin layer coated into a porous substrate of known pore size.

The mean pore sizes obtained by this method are compared with maximum pore size obtained by the measurement of the critical pressure in Table III. If ideal liquids which do not affect a membrane are used, the maximum pore size by the critical pressure measurement should yield identical values with different liquids. The stability of a membrane against the wetting liquid affects the values obtained by the method. The results also indicate the effect of perturbation of pore size by the testing method. The gas permeability method provides the advantage of the least perturbation and a useful means to investigate porous polymeric membranes.

TABLE III
Comparison of Mean Pore Size and Maximum Pore Size
Calculated from Critical Capillary Pressure

Membrane	Mean N ₂ pore size, μm	Maximum pore size, μm	
		By isobutyl alc.	by H ₂ O
Millipore VS	0.030	0.084	0.12
Millipore VM	0.043	0.090	0.13
Millipore VC	0.100	0.125	0.21
Polysulfone 1	0.052	0.060	0.07
Polysulfone 2	0.100	0.110	0.12

The absolute numerical values of pore size, particularly as a measure of cut-off size of filtration process, should be interpreted cautiously, depending on whether the membrane is used in gas, vapor, or liquid phase, since most polymeric porous membranes are not absolutely inert to the environmental effect.

Factors of Preparation that Influence Pore Size of Porous Polysulfone Membranes

The estimate of mean pore size made by using gas permeability data was applied to investigate the effect of factors involved in the preparation procedure of forming porous polysulfone membranes. Among factors that might influence the mean pore size of porous polysulfone membranes, the concentration of casting solution (DMF as the solvent), casting thickness (wet thickness), and the temperature of the coagulation bath are chosen as the major factors, and membranes are designed by these three factors using six-digit numbers. The first two digits refer to the concentration in per cent by weight of polymer in casting solution, the second two digits, to the casting thickness in mils (thousands of an inch), and the last two digits to the temperature of coagulation bath in °C. For instance, a membrane designated as 160500 indicates that the membrane was cast from 16% solution using a 5-mil casting thickness and was coagulated in a water bath at 0°C.

Once the value of m is determined, it is possible to estimate ϵ/q^2 of the membrane from eq. (3) or eq. (4) (see Appendix). Although it is possible to further estimate ϵ by assuming a certain value of q , or q by using value of ϵ obtained from other measurements, ϵ/q^2 seems to be a better parameter to characterize transport properties of a membrane because both ϵ and q are kinetic parameters so far as the transport properties of the membrane are concerned. In other words, pores with dead ends do not contribute to the transport properties of the membrane, and any static measurement to estimate ϵ does not distinguish through-pores and dead-end pores. If a constant value of q is assumed, the meaning of the tortuosity factor itself is lost. Therefore, m and ϵ/q^2 may be used as main parameters to characterize porous membranes. Results obtained with porous polysulfone microporous membranes are summarized in Tables IV through VI, using m and ϵ/q^2 as parameters to characterize porous membranes.

The properties of porous polymer membranes prepared by the coagulation process are governed by the precipitation rate, which is dependent on the rate of flow of solvent out of the cast polymer film and the rate of penetration of water into the precipitating front of the cast polymer film as

TABLE IV
Effect of Coagulating Bath Temperature on Properties
of Microporous Polysulfone Membranes

Membrane series no.	Dry thickness $\times 10^3$, cm	Pore size, μm	$(\epsilon/q^2) \times 10^2$	Water flux, ^a gfd	Compaction factor
160500	2.5	0.025	39.8	133	13.7
160515	2.8	0.045	25.1	96	16.2
160530	3.1	0.115	11.5	89	24.0
160700	4.3	0.08	18.1	156	16.0
160715	4.5	0.22	15.4	107	38.0
160740	5.6	0.50	16.0	92.5	55.0

^a Steady-state water flux (after compaction).

TABLE V
Effect of Wet Casting Thickness on Properties of
Microporous Polysulfone Membranes

Membrane series no.	Dry thickness $\times 10^3$, cm	Pore size, μm	$(\epsilon/q^2) \times 10^2$	Water flux, ^a gfd	Compaction factor
140512	2.8	0.06	27.3	92.5	23.2
140712	3.8	0.08	27.8	96.0	26.1
140912	4.7	0.12	16.2	122.0	31.7
160513	3.1	0.04	35.1	96.0	26.0
160713	4.1	0.05	31.6	70.4	31.5
160913	5.1	0.10	16.4	63.0	35.0

^a Steady-state water flux (after compaction).

TABLE VI
Effect of Polymer Concentration on Properties of
Microporous Polysulfone Membranes

Membrane series no.	Dry thickness $\times 10^3$, cm	Pore size, μm	$(\epsilon/q^2) \times 10^2$	Water flux, ^a gfd	Compaction factor
140512	2.8	0.055	32.5	116	23.2
160512	3.1	0.040	30.4	111	14.0
180512	3.2	0.038	24.1	81.5	9.0
230513	4.0	—	—	51.7	3.0
140900	6.3	0.10	30.2	166.2	17.3
150900	6.6	0.09	28.6	107.1	16.0
160900	7.4	0.07	27.3	100.0	12.7

^a Steady-state water flux (after compaction).

reported by Frommer and Lancet.⁴ Therefore, the temperature of the coagulation bath should have an important effect on the pore size of porous membranes.

Results obtained with membranes that were cast under identical conditions but coagulated at different temperatures are summarized in Table IV. The logarithm of mean pore sizes and the compaction factors are plotted against $1/T$ in Figures 4 and 5, respectively. As can be seen in these figures, pore size and compaction factor both follow a typical Arrhenius plot. Under conditions used in these experiments (total amount of polymer

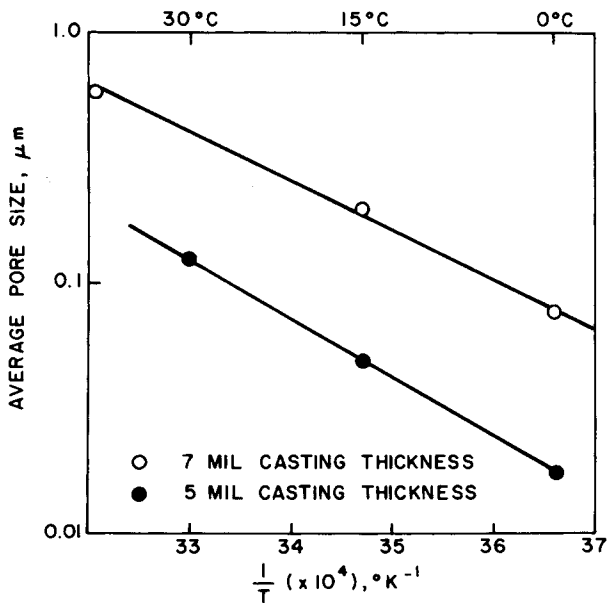


Fig. 4. Mean pore size of microporous polysulfone membranes as a function of temperature of coagulation bath (water). Casting solutions, 16% polymer in DMF.

in a given area being constant), the larger pore size should result in more bulky membranes, which have a higher tendency of compacting under high pressure. The thickness of membrane (shown in Table IV), pore sizes, and compaction factors are in good accordance with process of coagulation.

The decrease of ϵ/q^2 with increasing coagulation temperature despite of increasing pore size indicates that coagulation at higher temperature tends to produce larger sized pores but fewer numbers of pores in a unit area of membrane. This aspect and the bulkiness in the direction of membrane thickness are responsible for the decrease of the steady-state water flux (after compaction occurred) with increasing pore size of the membranes.

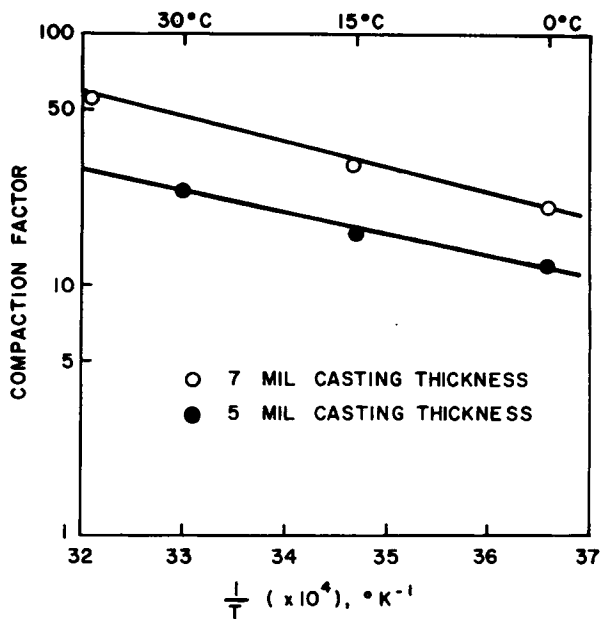


Fig. 5. Compacting factors of microporous polysulfone membranes as a function of temperature of coagulation bath (water). Casting solution, 16% polymer in DMF.

The effect of casting thickness and the influence of polymer concentration is summarized in Tables V and VI, respectively. These data compare membranes that have varying amount of polymer, due to different casting thickness in the former case and due to different concentrations of casting solution in the latter case. The increasing amount of polymer, either due to larger casting thickness or due to higher polymer concentration in the casting solution, tends to decrease the values of ϵ/q^2 .

The larger casting thickness increases the pore size, whereas the higher concentration decreases the pore size. This opposing trend may be due to higher viscosity of casting solution with higher concentration, which decreases the mobility of polymer and increases the resistance of solvent removal.

Figure 6 shows the steady decrease of pore size with increasing concentration of polymer in the casting solution. The compaction factor of membranes is also influenced by the concentration of polymer in the casting solution, as shown in Figure 7. The compaction factor decreases with increasing polymer concentration (increasing membrane thickness), which is also opposite to the trend found with membrane cast at various casting thicknesses.

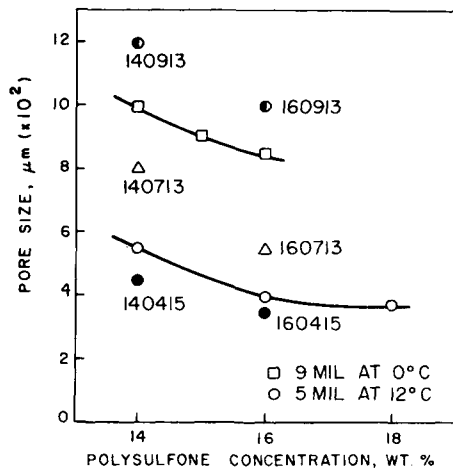


Fig. 6. Dependence of mean pore size of microporous polysulfone membranes on the polymer concentration of casting solution (in DMF).

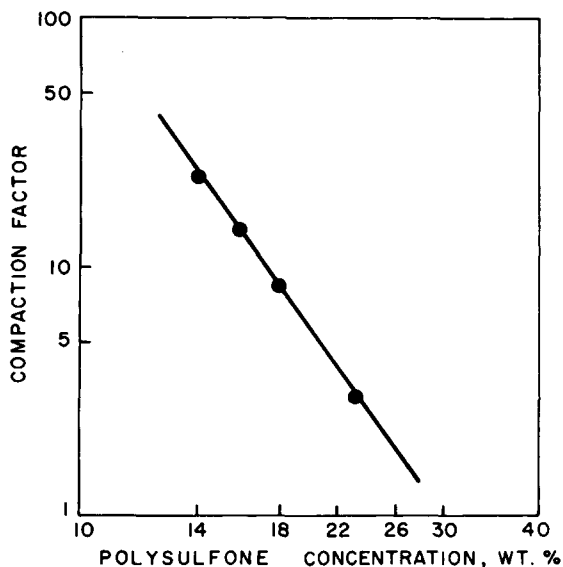


Fig. 7. Dependence of compaction factor of microporous polysulfone membrane on polymer concentration of casting solution (in DMF). Casting thickness, 5 mils; coagulation temperature, 12°C.

The influence of solvents in the coagulation bath is shown in Table VII. With the presence of DMF in the coagulation bath, the pore size of a membrane is slightly higher than that of a membrane coagulated in pure water at the same temperature. However, a significant increase in water flux with minimized compaction factor results compared to membranes of comparable pore size that are coagulated in a bath without DMF at different temperature. The addition of methanol into the coagulation bath resulted in much larger pore sizes.

TABLE VII
Effect of Additives in Coagulating Bath on
Properties of Microporous Polysulfone Membranes^a

Concentration,	Pore size, μm	Water flux, ^b gfd	Compaction factor
pure water	0.025	133	3.6
DMF 0.2	0.035	170	8.1
DMF 1.0	0.045	222	5.0
MeOH 10.0	0.120	220	18.5
MeOH 20.0	0.100	275	9.0

^a Series no. 160500.

^b Steady-state water flux (after compaction).

Although considerable increase in the initial water flux of porous membranes can be obtained by increasing the mean pore size, the high water flux may not be utilized if the membrane is used under high pressure. The difference among the steady-state water fluxes (after membranes have compacted under 500 psi) is not as great as observed in the initial water flux. This implies that, depending on the conditions in which a membrane is used, the mean pore size should be cautiously interpreted. The pore size of a membrane decreases after it is subjected to hydraulic pressure of 500 psi. Some results of pore size decrease due to compaction are shown in Table VIII.

These results may be qualitatively explained by the mechanism of coagulation process developed by studies^{4,5} of Loeb-Sourirajan-type cellulose acetate membranes in which the rate of solvent removal and the rate of

TABLE VIII
Pore Size Change Due to Compaction of Microporous Polysulfone Membranes^a

Membrane series no.	Pore size, μm	
	Before	After
160713	0.06	0.02
160730	0.26	0.08
160740	0.50	0.16
160900	0.08	0.07
160912	0.10	0.07

^a A membrane was subjected to water flux test under 500 psi for 24 hr.

water moving into a cast membrane play important roles. Factors that increase the rate of water moving into a cast membrane will increase the pore size. Water is a much stronger coagulating agent to polysulfone than it is to cellulose acetate, and the minimum pore size obtainable with coagulated polysulfone is consequently much larger than those with cellulose acetate. Nevertheless, many factors influence the results in a similar fashion, and the pore size can be controlled to tailor the properties of microporous membranes.

These results indicate the following trends: pore size is increased by (1) increasing casting thickness, (2) increasing temperature of coagulation bath, and (3) decreasing concentration of polymer in the casting solution.

The effective porosity represented by ϵ/q^2 increases with (1) decreasing casting thickness, (2) decreasing temperature of coagulation bath, and (3) decreasing concentration of polymer in the casting solution.

The water flux through the membrane is influenced by pore size, porosity, and the membrane thickness and is not always proportional to the pore size.

The smaller compaction factor seems to be correlated to the smaller pore size and the larger value of ϵ/q^2 .

Porous polysulfone membranes which have high water flux, small compaction factor, and smaller pore size can be obtained by the combination of (1) higher concentration of casting solution, (2) smaller casting thickness, and (3) lower temperature of coagulation bath.

The method of pore size determination described in this paper provides a very useful means of investigating properties of microporous membranes and its application can be extended to wide varieties of porous polymer membranes in different membrane forms such as tubular and hollow fiber membranes.

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References

1. H. Yasuda and C. E. Lamaze, *J. Macromol. Sci.—Phys.*, **B5**(1), 111 (1971).
2. P. G. Carman, *Flow of Gases Through Porous Media*, Butterworth, London, 1956.
3. E. J. Hopfinger and M. Altman, *J. Chem. Phys.*, **50**, 2417 (1969).
4. M. A. Frommer and D. Lancet, *Reverse Osmosis Membrane Research*, Plenum Press, New York, 1971, pp. 85–110.
5. H. Strathman, P. Scheible, and R. W. Baker, *J. Appl. Polym. Sci.*, **15**, 811, t971.

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