paring true liquid holdup data from two different pipe diameters, we can determine that the mixture Froude numbers adequately account for variations in pipe diameter, and any additional diameter effect is minimal when using the data correlation of $\eta$ vs. $\lambda$ at various angles of inclinations using mixture Froude number as a parameter for pipe diameters greater than 2.54 cm.

Finally, based on this extrapolative technique and data from Guzhov et al. (1967), a correlation has been developed which proved to be most reliable for predicting true liquid content for inclined slug flows. Since the correlation has been tested with pipe diameters up to 7.94 cm, it is recommended for general use with those traditional reservations regarding the character of the gas-liquid system. That is, all the data used in this work and those data used to test the proposed correlation were based on the air-water system, and for general use, this correlation should be tested with other gas-liquid systems.

### NOTATION

$A$ = pipe cross-sectional area, cm$^2$
$C_1$, $C_2$ = constants in Equations (1) and (2), respectively
$D$ = pipe diameter, cm
$f(\theta)$ = some function of angle of inclination
$Fr_m$ = mixture Froude number, $U_{NS}^2/Dg$
$g$ = gravitational constant
$Q_G$, $Q_F$ = gas and liquid flow rates, respectively, cm$^3$/s
$U_{NS}$ = no-slip or mixture velocity, $Q_G + Q_F/A$, cm/s
$U_{BR}$ = bubble rise velocity given by Equation (2), cm/s

#### Greek Letters

$\alpha$ = gas void fraction
$\eta$ = true liquid holdup, fraction
$\eta_{\lambda=0}$ = true liquid holdup at zero liquid rate
$\theta$ = angle of inclination from the horizontal
$\lambda$ = input liquid quality, $Q_F/Q_F + Q_G$

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# An Unsteady State Method for Measuring the Permeability of Small Tubular Membranes

An experimental method is described for measuring the permeability of small tubular (hollow fiber) membranes by means of an unsteady state diffusion experiment. Permeability data obtained by this method are reported for experimental collagen and commercial cellulose acetate membranes for urea, sucrose, and polyethylene glycol (MW ~ 4 000).

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# SCOPE

The goal of the work described here is the development of a convenient and accurate method for measuring the permeability of small tubular membranes. One use of this method is to determine the composition and processing conditions which give the desired membrane permeability for a particular application, such as the artificial kidney (Krueger, 1974). The method can also be used to detect any changes in membrane properties following the use of a mass transfer device, for example, determination of changes in membrane permeability with repeated use and sterilization of an artificial kidney. Other uses include quality control during manufacturing, the generation of data for modeling mass transfer devices, and the evaluation of available membranes for specific applications.

The mathematical solution of the unsteady state diffusion problem in a long composite cylinder with interfacial resistances and a computational procedure for evaluating the solution are given in a previous paper (Stevenson, 1974). This solution can also be obtained from a more general analysis given by Ölçer (1968) when a misprint noted by Stevenson (1974) is corrected. For the case of no mass transfer resistance at the inner radius of the cylinder, the solution by Stevenson (1974) is a special case of a general analysis by Shperling (1972).*

A numerical procedure for analyzing a similar problem, unsteady state diffusion with nonlinear adsorption in a composite cylinder, is given in a paper by Crank and Godson (1947).

The use of unsteady state heat conduction and diffusion experiments to evaluate material properties is discussed in books by Carslaw and Jaeger (1959), Crank (1956), Jost (1960), and Crosby (1961). Satterfield et al. (1973) and others cited in their article have used unsteady state experiments to study restricted diffusion within fine pores. In an experiment similar to the one described here, Mayhan et al. (1970) determined the thermal conductivity of a protective coating on a metal cylinder by matching their experimental measurements of center line temperature to the solution of the unsteady state heat conduction problem in a composite cylinder (Jaeger, 1941).

# CONCLUSIONS AND SIGNIFICANCE

The feasibility of using an unsteady state diffusion experiment to measure the permeability of small tubular membranes is demonstrated.

The experiment is shown to be free from large systematic errors caused by a mass transfer resistance at the interface between the membrane tube and the surrounding bath, and by convective mixing in the presumably stagnant solution enclosed by the membrane tube.

Approximate values for the (steady state) permeability of experimental collagen and commercial cellulose acetate membranes are reported for urea, sucrose, and polyethylene glycol (MW ~4 000).

The conventional method for determining the permeability of tubular membranes (Leonard, 1974) involves the construction of a small-scale dialyzer and the measurement of overall mass transfer resistances. The method is subject to errors caused by convective transport of solute through the membrane and requires the production and potting of a large number of tubular membranes. It is also necessary to evaluate the mass transfer resistances at the fluid-membrane interfaces. The method proposed here is not subject to these drawbacks and should be more convenient than the conventional method.

The unsteady state method will indicate the existence of significant solute-membrane binding, but the data analysis is complicated when binding occurs (Weisz, 1967; Weisz and Hicks, 1967).

## MATERIALS

### Membranes

Small tubular (hollow fiber) membranes made of two different materials were used in the experiments reported here. Cellulose acetate membranes (Dowex Permeator Fibers, HFA1-01, CA-$c_1$) were obtained from the Dow Chemical Company, Walnut Creek, California. Experimental collagen membranes (HF-739, HF-740) prepared by the Japan Leather Company, Tokyo, Japan, were obtained through the Rogosin Kidney Center, Cornell Medical Center, New York, New York. The collagen membranes were prepared by extruding a 2.5% by weight enzyme solubilized collagen solution into a sodium chloride saturated coagulation bath. The membranes were cross-linked with ultraviolet light for 5 min. Lot HF-740 was aged at room temperature for 1 mo. to stabilize the membrane properties (Stenzel et al., 1974). Lot HF-739 was aged at 110°C for 3 hr.

### Solutes

The test solutes used in this study were urea, sucrose, and polyethylene glycol (PEG), (MW ~ 4 000). All solutes were radioactive $C^{14}$ labeled compounds obtained from New England Nuclear Corporation. These solutes were selected to cover a range of molecular weights and have been used previously by Colton et al. (1971) in a permeability study of cellulosic membranes.

Values of the diffusivity $D_1$ for these solutes at 37°C in water and/or isotonic saline solution were obtained from the literature, by an unsteady state diffusion experiment in a 0.5% by weight collagen gel (Von Deak, 1975), and by use of a diaphragm diffusion cell with well-characterized mica membranes (Malone, 1975). These values are tabulated in Table 1.

No evidence was found for solute-membrane binding between urea, sucrose, and PEG and the membranes used in this study. However, equilibration experiments showed that dextran (MW ~ 15 000 to 17 000) binds to both collagen and cellulose acetate membranes and that Vitamin $B_{12}$ binds to collagen membranes (Weinberg, 1974).

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* The English translation of Shperling's article contains two misprints. The first term on the right-hand side of Equation (15) should be multiplied by $r_1$, and the correct version of Equation (34) can be obtained easily from Equation (32).

TABLE 1. SOLUTE DIFFUSIVITIES AT 37°C

| Solute | Molecular weight | Literature values, cm²/s × 10⁵ | Measured values, cm²/s × 10⁵ | Value used in this study, cm²/s × 10⁵ |
|---|---|---|---|---|
| Urea | 60.06 | 1.81[*] (Longsworth, 1954)<br>1.84[†] (Colton et al., 1970) | 1.80[*] (Von Deak, 1975) | 1.81 |
| Sucrose | 342.3 | 0.697[*], [**] (Longsworth, 1953)<br>0.711[†] (Colton et al., 1970) | | 0.697 |
| Polyethylene glycol | 4,000 | 0.227[†] (Colton et al., 1971) | 0.197[*] (Von Deak, 1975)<br>0.196[†], [**] (Malone, 1975) | 0.196 |

[*] In water.
[†] In isotonic saline solution.
[**] Extrapolated to 37°C with $D\mu/T$ = const.

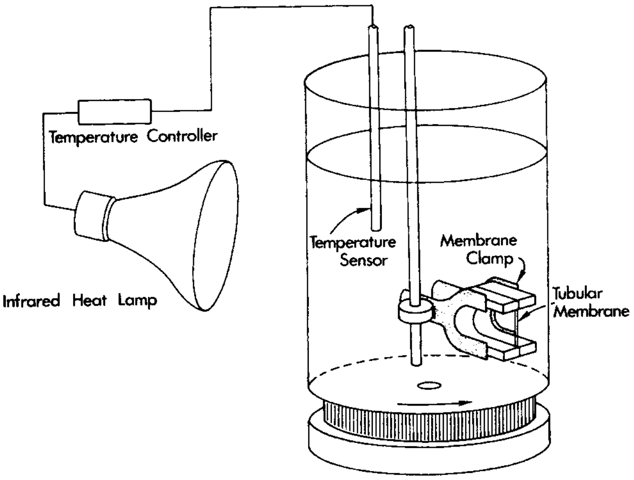

Fig. 1. Schematic diagram of experimental apparatus.

## PERMEABILITY MEASUREMENTS

### Equipment

Membrane permeability was measured by an unsteady state diffusion experiment in which a sealed membrane tube was first equilibrated with a solute and then exposed to a solute-free rotating bath for a predetermined time. The experimental equipment is shown in Figure 1.

The rotating bath was fabricated from a polymethylmethacrylate[*] cylindrical tube 16.5 cm in inside diameter and 22.8 cm in height. The bath was driven by an electric motor through a variable speed gear at angular velocities ranging up to 168 rev/min. The bath was filled with approximately 3 l of isotonic saline solution which was changed with sufficient frequency to prevent the accumulation of radioactive solutes.

The temperature of the rotating bath was maintained at 37° ± 0.5°C by means of an infrared lamp connected to a temperature controller.

During experimental runs, short sections of membrane tube were held in place by two U shaped pieces of polymethylmethacrylate. The pieces of plastic were cemented to a spring clamp which closed with sufficient force to seal the ends of a membrane tube positioned between them (Figure 1). The length of the exposed portion of the membrane between the clamps was 2.5 cm. The crimping of the membrane by the clamp extended less than one membrane diameter away from the clamp. The small percentage change in the mass transfer rate resulting from this crimping is probably nearly independent of exposure time and therefore has very little effect on the semilog graphs (for example, Figure 3) used to determine permeability.

Concentrations of radioactive solutes were determined by liquid scintillation counting with a Packard Tri-Carb Scintillation Spectrometer, Model 3002. The scintillation medium was 20 ml of Bray's solution (Bray, 1960), and the water content of the sample to be counted did not exceed 0.1 ml.

### Procedure

The procedure for conducting the unsteady state diffusion experiment is outlined below and is described in more detail by Von Deak (1975) and Weinberg (1974).

To remove plasticizers or residual processing chemicals, long sections of the tubular membranes were soaked for at least 24 hr. in an isotonic saline solution containing sodium azide as a bacteriocide.

After the membranes were soaked they were cut into shorter lengths and equilibrated with the desired radioactive solute in an isotonic saline solution containing 0.02% by weight sodium azide.

A 3 cm length of equilibrated membrane was then carefully secured in the clamp without bowing or stretching the membrane. Excess solute was removed by exposing the clamped membrane to a flat water jet for less than 1 s.

In each series of experimental runs with a particular solute, two of the clamped membranes were used to determine the amount of solute initially present, and each of the remaining clamped membranes were attached in turn to a brass rod and suspended at a fixed position near the wall of the rotating bath. The axis of the membrane was parallel to the axis of rotation of the bath. The flow approaching the membrane approximated a uniform parallel velocity normal to a cylinder. This velocity was sufficiently large so that the mass transfer resistance at the membrane-bath interface was negligible. The clamped membrane was not visibly bowed or vibrated by the flow.

After a clamped membrane was removed from the bath, the membrane was carefully cut from the clamp with a scalpel and placed in the Bray's solution. The amount of solute remaining in each of the sealed membrane tubes was determined by scintillation counting.

The inside and outside radii ($a$ and $b$, respectively) of the wet membrane tubes were measured by observing the membrane through a microscope.

The volume fraction water in a wet membrane $\epsilon$ was determined by making the measurements indicated by

$$\epsilon = 1 - \frac{M_2 + M_3 - M_1}{V_m \, \rho_{H_2O}} \qquad (1)$$

where $M_1$ is the mass of a pycnometer filled with water and membranes, $M_2$ is the mass of the pycnometer filled with water only, $M_3$ is the mass of the same membranes after drying in a vacuum at 25°C, and $V_m$ is the volume of the wet membrane tubes determined from measurements through a microscope. The accuracy of $\epsilon$ determined in this manner is estimated to be ± 6%.

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[*] Plexiglas.

### Data Analysis

In analyzing this experiment we first computed an unsteady state permeability $P_u$ directly from the experimental data and then used an approximate relation to convert $P_u$ to the conventional (steady state) membrane permeability $P_s$. The mathematical basis for this analysis was given previously by Stevenson (1974).

The first step in this procedure is plotting ln $(R)$ vs. $\tau$, where $R$ is the fraction of solute remaining in the sealed membrane tube after a time $t$ in the rotating bath, and $\tau$ is a dimensionless time given by $tD_1/b^2$. As $\tau \to \infty$, the slope of the ln $(R)$ vs. $\tau$ curve approaches a negative constant. This asymptotic value of the slope is related to the first root $\alpha_1$ of Equation (13) in Stevenson (1974) by

$$\lim_{\tau\to\infty} \frac{d\ln(R)}{d\tau} = \lim_{\tau\to\infty} \text{slope} = -(\alpha_1)^2 \qquad (2)$$

For typical experimental conditions, the slope is within 2% of its asymptotic value when $\tau > 0.35$.

For the purpose of analyzing experimental data, a convenient definition for the membrane permeability $P$ is given by (Equation (22) of Stevenson, (1974):

$$P \equiv \frac{\dot{M}|_{r=a}}{(2\pi bL)[C_1(a) - C_1(b)]} \qquad (3)$$

where $\dot{M}$ is the radial solute flow (moles/s), $2\pi bL$ is the area of the membrane evaluated at the outer radius, and $C_1(a) - C_1(b)$ is the concentration difference (based on the external solutions) across the membrane tube. The assumption of a negligible mass transfer resistance at the outer radius of the membrane means that $C_1(b)$ is also the concentration in the solution surrounding the membrane.

If both $C_1(a)$ and $C_1(b)$ are constant, and the solute flow $\dot{M}$ has attained a steady state value, the steady state permeability $P_s$ is given by Equation (23) Stevenson (1974):

$$\frac{P_s b \ln(1/\kappa)}{D_1} = \frac{D_2K}{D_1} = \frac{D_{\text{eff}}}{D_1} \qquad (4)$$

where $D_2$ is the diffusivity within the membrane (based on concentrations within the membrane), and $K$ is the equilibrium partition coefficient. The product $KD_2$ is sometimes called the effective diffusivity $D_{\text{eff}}$ in the membrane (based on concentrations in the external solutions). For a given solute, $D_{\text{eff}}$ is an intrinsic property of the membrane material and accordingly is a useful parameter for comparing different materials.

For the unsteady state experiments described in this paper, Equation (3) can be used to define an unsteady state permeability for which both $\dot{M}$ and $C_1(a)$ are time dependent. At large values of the time, this unsteady state permeability approaches a time-independent asymptotic value $P_u$ given by Equation (26) of Stevenson (1974):

$$\frac{P_u b \ln(1/\kappa)}{D_1} = \frac{\kappa\alpha_1 J_1(\kappa\alpha_1)\ln(1/\kappa)}{J_o(\kappa\alpha_1)} \qquad (5)$$

where $J_o$ and $J_1$ are Bessel functions of the first kind. The asymptotic value of the slope of the ln$(R)$ vs. $\tau$ curve was determined by a least-square regression analysis (Draper and Smith, 1966), and the value of $\alpha_1$ was determined as indicated by Equation (2).

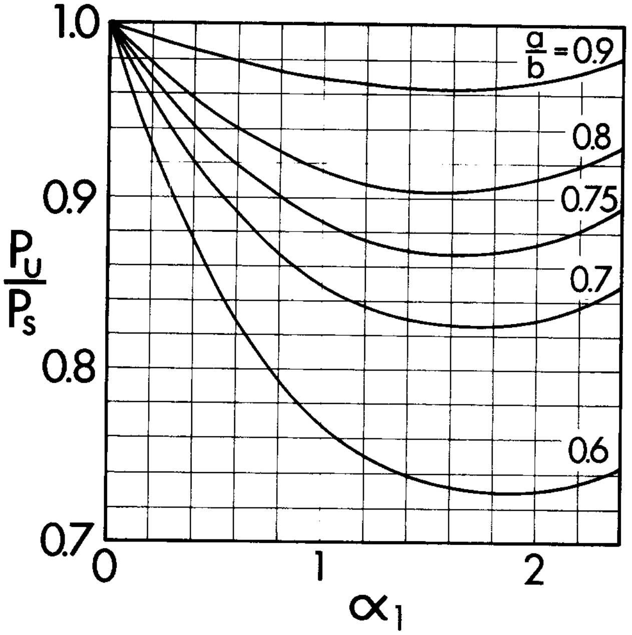

Fig. 2. Conversion factor graph relating $P_u/P_s$ to experimentally measured parameters $\alpha_1$ and $a/b$. This graph is based on Equations (4) and (5) and the relation between $D_1/D_2$ and $K$ given by Equation (8).

Because $D_{\text{eff}}/D_1$ or $P_s$ are commonly used for membrane comparisons and for design purposes, a relation between these parameters and the experimentally measured $P_u$ would be useful. When interfacial mass transfer resistances are negligible, we know that for a given membrane and solute (Stevenson, 1974)

$$\frac{P_u}{P_s} = \text{function of } (D_1/D_2, K, \kappa) \qquad (6)$$

and

$$\alpha_1 = \text{function of } (D_1/D_2, K, \kappa) \qquad (7)$$

Since it is not convenient to measure $D_1/D_2$ and $K$, we want to reduce the functional dependence of $P_u/P_s$ from the three variables indicated in Equation (6) to two variables ($\kappa$, $\alpha_1$) which we can measure easily. One way to achieve this reduction is to find a relation between $K$ and $D_1/D_2$ which is approximately valid for membranes of interest. By analyzing 32 experimental measurements of $K$ and $D_1/D_2$ obtained by Colton et al. (1971) for Cuprophane PT-150 and Avisco wet gel cellophane, by Farrell and Babb (1973) for Cuprophane PT-150, by Kaufmann and Leonard (1968) for DuPont cellophane, and by the authors of this paper for collagen, we obtained the following approximate expression relating $K$ and $D_1/D_2$:

$$\frac{D_1}{D_2 K} + 3.7 = 4.7\, K^{-2.22} \qquad (8)$$

The average deviation between predicted values of $D_2K/D_1$ and experimental measurements of $D_2K/D_1$ was 18%. The predictions for $D_2K/D_1$ given by Equation (8) were usually low for urea and high for sucrose.

Although Equation (8) is empirical and based on data for relatively few membranes, the equation does provide a reasonable basis for computing a relation between $P_u$ and $P_s$. By specifying $\kappa$ and values of $D_1/D_2$ and $K$ consistent with Equation (8), we can calculate $\alpha_1$ and $P_u/P_s$ using Equations (13), (23), and (26) in Stevenson (1974). A plot of $P_u/P_s$ vs. $\alpha_1$ with $\kappa$ $(= a/b)$ as a parameter is shown in Figure 2. An approximate value for $P_s$ can be obtained by evaluating $P_u$ by using Equation (5) and then by dividing $P_u$ by the conversion factor $[P_u/P_s]$ obtained from Figure 2 for the known values of $\alpha_1$ and $\kappa$. An assessment of the error in evaluating $P_s$ from $P_u$ by using Figure 2 was made for the experimental values of $D_1/D_2$ and $K$ which showed the largest deviations (35 to 62%) from Equation (8). In this analysis the maximum error in the value of $P_s$ resulting from the use of Figure 2 was 4%.

### Error Analysis

The value of $P_u\, b \ln(1/\kappa)/D_1$ computed from Equation (5) is subject to random errors resulting from the evaluation of $\alpha_1$ and $\kappa$ from experimental data. An error analysis on Equation (5) indicated that $P_u\, b \ln\,(1/\kappa)D_1$ is much more sensitive to small percentage errors in $\alpha_1$ than to small percentage errors in $\kappa$. Therefore, the 95% confidence limits on the precision of $P_u\, b \ln(1/\kappa)/D_1$ were calculated with the assumption that random errors in $P_u\, b \ln(1/\kappa)/D_1$ were due solely to random errors in the evaluation of $\alpha_1$. The 95% confidence limits on $\alpha_1$ were determined from the 95% confidence limits on the asymptotic value of the slope given by Equation (2). Standard statistical techniques (Draper and Smith, 1966) were used to compute the slope and its 95% confidence limits from the $R(\tau)$ data.

In addition to random errors, systematic errors in the evaluation of $b$, $L$, $\kappa$, $D_1$, $t$ and $R$ affect the accuracy of $P_u\, b \ln(1/\kappa)/D_1$. Although difficult to assess, these errors deserve some comment.

A cross sectional view showed that the wall thickness of some of the cellulose acetate membranes varied by nearly a factor of 2. The largest possible error in $\alpha_1$ resulting from this variation in wall thickness will occur when all the resistance to diffusion is located in the tube wall, or, equivalently, the solution enclosed by the membrane is well stirred. The maximum error in $\alpha_1$ was estimated in the following way. The steady state resistances to diffusion through the membrane were evaluated for membrane geometries formed by appropriate surfaces of the cylindrical (constant wall thickness) and the bipolar (variable wall thickness) coordinate systems (Carslaw and Jaeger, 1959, p. 451). These resistances were substituted into a quasi steady state analysis of diffusion through a membrane tube enclosing a well-stirred solution. This analysis showed that the maximum possible error in $\alpha_1$ would be less than 4%, and the maximum expected error in $P_u\, b \ln(1/\kappa)/D_1$ would be less than 9%.

An error analysis of Equation (5) showed that, on a percentage basis, the dimensional unsteady state permeability $P_u$ is relatively insensitive to errors in $D_1$ for low values of $D_1$ which are most prone to errors in experimental measurement. For example, when $\kappa\, \alpha_1 < 0.83$ (small $D_1$), a 10% error in $D_1$ results in an error of less than 1% in $P_u$.

## VALIDATION EXPERIMENTS

Two assumptions made in the mathematical analysis of this experiment (Stevenson, 1974) are the absence of convective mixing in the solution enclosed by the membrane tube, and the insignificance of the mass transfer resistance at the interface between the membrane and the external solution.

### Absence of Convective Mixing

The mathematical analysis of this experiment is restricted to mass transfer by diffusion both in the membrane tube and in the enclosed solution. Here we want to determine if convective mixing in the enclosed solution could introduce a significant experimental deviation from the mathematical analysis. This convective mixing could be caused by unobservable vibrations of the membrane induced by the external flow.

To make this determination, a series of unsteady permeability measurement experiments were conducted with urea and collagen membranes. The experiments were carried out at 22°C but otherwise as described above except that in one-half of the experiments the membrane tubes were filled with a 0.5% by weight solution of agar (Bacto-Agar, Difco Laboratories, Detroit, Michigan). This gel was firm enough to eliminate the possibility of convective mixing yet dilute enough to have a negligible effect on the diffusion of small molecules (Lauffer, 1961).

The rationale for selecting urea and collagen for this study is as follows. Because $D_{\text{eff}}/D_1$ is approximately 0.45 for the diffusion of urea in collagen membranes, the average concentration gradient in the (assumed) stagnant enclosed solution is about one-half of the concentration gradient in the membrane. Therefore, if the concentration gradient in the solution were eliminated by convective mixing, we would expect a large change in the $R(\tau)$ curve. On the other hand, for the diffusion of PEG in collagen, $D_{\text{eff}}/D_1$ is approximately 0.1, and the average concentration gradient in the enclosed solution is about one-tenth of the concentration gradient in the membrane. Accordingly, we would not expect the elimination of this small gradient by convective mixing to alter the $R(\tau)$ curve significantly. Since collagen is the most permeable material used in this study, the value of $D_{\text{eff}}/D_1$ for any given solute will be largest for collagen membranes. Hence, the potential effect of convective mixing should be largest for the diffusion of urea in collagen membrane tubes.

For typical membrane constants characterizing the diffusion of urea in collagen ($K = 0.89$, $\kappa = 0.77$, and $D_1/D_2 = 2.1$), the mathematical solution given by Jaeger (1940) and cited by Crank (1956, p. 80) can be used to determine the asymptotic slope of the ln $(R)$ vs. $\tau$ curve when the solution enclosed by the tubular membrane is well stirred. [These references contain a misprint as noted by Stevenson (1974).]

This analysis showed that complete convective mixing in the enclosed solution would increase the apparent value of $D_{\text{eff}}/D_1$ by 55%. From among the first five entries in Table 2 it can be seen that the percentage changes in $D_{\text{eff}}/D_1$ for an enclosed solution relative to an enclosed gel are +18 and −12%. These results indicate that convective mixing does not have a significant effect on the experimental measurements.

### Insignificance of Interfacial Resistance

In the analysis of experimental data it is assumed that the solute concentration at the outer radius of the membrane is in equilibrium with the solute concentration in the external solution. For this assumption to be valid, the mass transfer resistance at the interface between the membrane and external solution must be negligible. This assumption is assessed below by mathematical simulations of the unsteady state experiment in which the mass transfer resistance at the membrane-solution interface is varied from zero to the largest values expected in an actual experiment.

The mass transfer coefficient at the interface was calculated for typical experimental conditions by adapting a heat transfer correlation for flow normal to cylinders (Bennett and Myers, 1962, p. 341, and Bird et al., 1960, p. 646)

$$Sh = \frac{k_b\, 2b}{D_1} = 0.677\, Re^{0.466}\, Sc^{1/3} \tag{9}$$

which is valid in the Reynolds number range $40 < Re < 4\,000$. Ordinarily, permeability measurement experiments were performed at 37°C, and the fluid velocity normal to the membrane was 70 cm/s. This fluid velocity was attained by rotating the bath at 10 rad/s and by locating the membrane 7 cm from the axis of rotation. A flow

Table 2. Permeabilities of Tubular Membranes
Collagen Membranes

| Lot No. | Solute | Temp., °C | $\bar{b}$, cm | $\bar{\kappa}$ | $\alpha_1$ (95% CL) | $\frac{P_u b \ln(1/\kappa)}{D_1}$ (95% CL) | $P_u$, $\frac{\text{cm}}{\text{s}} \times 10^4$ | $P_s$** $\frac{\text{cm}}{\text{s}} \times 10^4$ | $\frac{D_{eff}^{**}}{D_1}$ (95% CL) |
|---|---|---|---|---|---|---|---|---|---|
| 739* | Urea | 22 | 0.0400 | 0.800 | 1.86<br>(0.26) | 0.357<br>(0.151) | 5.00 | 5.52 | 0.394<br>(0.167) |
| 739 | Urea | 22 | 0.0405 | 0.802 | 1.97<br>(0.27) | 0.423<br>(0.188) | 5.93 | 6.52 | 0.465<br>(0.207) |
| 739 | Urea | 37 | 0.0358 | 0.747 | 1.83<br>(0.08) | 0.367<br>(0.045) | 6.38 | 7.34 | 0.422<br>(0.052) |
| 740* | Urea | 22 | 0.0404 | 0.773 | 1.99<br>(0.09) | 0.453<br>(0.066) | 5.43 | 6.10 | 0.509<br>(0.074) |
| 740 | Urea | 22 | 0.0406 | 0.778 | 1.91<br>(0.08) | 0.397<br>(0.050) | 4.87 | 5.48 | 0.447<br>(0.056) |
| 740 | Urea | 37 | 0.0402 | 0.771 | 1.83<br>(0.12) | 0.356<br>(0.065) | 6.16 | 6.97 | 0.403<br>(0.074) |
| 740 | Sucrose | 37 | 0.0415 | 0.783 | 1.77<br>(0.11) | 0.319<br>(0.053) | 2.19 | 2.46 | 0.358<br>(0.060) |
| 740 | PEG | 37 | 0.0418 | 0.803 | 1.14<br>(0.06) | 0.103<br>(0.013) | 0.218 | 0.239 | 0.113<br>(0.014) |
| | | | | Cellulose Acetate Membranes | | | | | |
| | Urea† | 37 | 0.0145 | 0.789 | 1.19<br>(0.11) | 0.119<br>(0.026) | 6.28 | 6.97 | 0.132<br>(0.028) |
| | Urea† | 37 | 0.0143 | 0.811 | 1.17<br>(0.13) | 0.108<br>(0.026) | 6.50 | 7.10 | 0.118<br>(0.028) |
| | Sucrose† | 37 | 0.0138 | 0.771 | 0.983<br>(0.097) | 0.0805<br>(0.0170) | 1.57 | 1.75 | 0.0896<br>(0.0189) |
| | Sucrose† | 37 | 0.0134 | 0.772 | 0.976<br>(0.071) | 0.0794<br>(0.0120) | 1.60 | 1.78 | 0.0883<br>(0.0133) |
| | PEG | 37 | 0.0137 | 0.781 | 0.707<br>(0.032) | 0.0392<br>(0.0040) | 0.227 | 0.249 | 0.0429<br>(0.0044) |

* Solution enclosed by membrane tube contained 0.5% agar gel.
** Obtained from $P_u$ by use of Figure 2.
† Duplicate runs by different investigators.

Table 3. Assessment of the Effect of Interfacial Mass Transfer Resistances on Experimental Measurements with Urea

| Membrane | $2b$, cm | $\kappa$ | $K$ | $\frac{D_1}{D_2}$ | $Sh$ | $\alpha_1$ | Percent error in $P_u$ due to assuming $Sh = \infty$ |
|---|---|---|---|---|---|---|---|
| Collagen 739 | 0.071 | 0.75 | 0.89 | 2.1 | 100 | 1.813 | 4 |
| | 0.071 | 0.75 | 0.89 | 2.1 | $\infty$ | 1.837 | |
| Cellulose acetate | 0.028 | 0.80 | 0.66 | 5.2 | 60 | 1.183 | 2 |
| | 0.028 | 0.80 | 0.66 | 5.2 | $\infty$ | 1.194 | |

visualization study with ink streak lines and a calculation of the boundary-layer thickness confirmed that a uniform fluid velocity existed along almost the entire length of the membrane.

Urea was selected as a solute for this assessment because it has the highest mass transfer rate out of the sealed membrane tube of any solute used in this study and hence is the most susceptible to the influence of a finite interfacial mass transfer resistance. Membrane constants and other parameters for the simulation were selected as follows. The dimensionless mass transfer coefficient $Sh$ was determined from Equation (9), the equilibrium partition coefficient K was set equal to the volume fraction water in the membrane, and $\kappa = a/b$ was determined from measurements through a microscope. $D_1/D_2$ was determined by matching the asymptotic values of the slopes of the simulated and experimental $\ln(R)$ vs. $\tau$ curves.

The results of these simulations are given in Table 3 and compared with experimental data in Figure 3. Because of the very close agreement between the simulations for an infinite mass transfer coefficient ($Sh = \infty$) and the estimated minimum value of the coefficient under experimental conditions, we conclude that the mass transfer resistance at the interface between the membrane and external solution is insignificant when compared to other mass transfer resistances.

## RESULTS

The following results for the volume fraction water in the membranes at room temperature were obtained by using the method described in a preceding section of this paper: collagen HF-739, $\epsilon = 0.89$; collagen HF-740, $\epsilon = 0.89$; and cellulose acetate, $\epsilon = 0.66$. The $\epsilon$ value for collagen HF-739 reported here is in reasonable agreement with the results obtained by other methods, $\epsilon = 0.88$ determined in a preliminary investigation by Stevenson

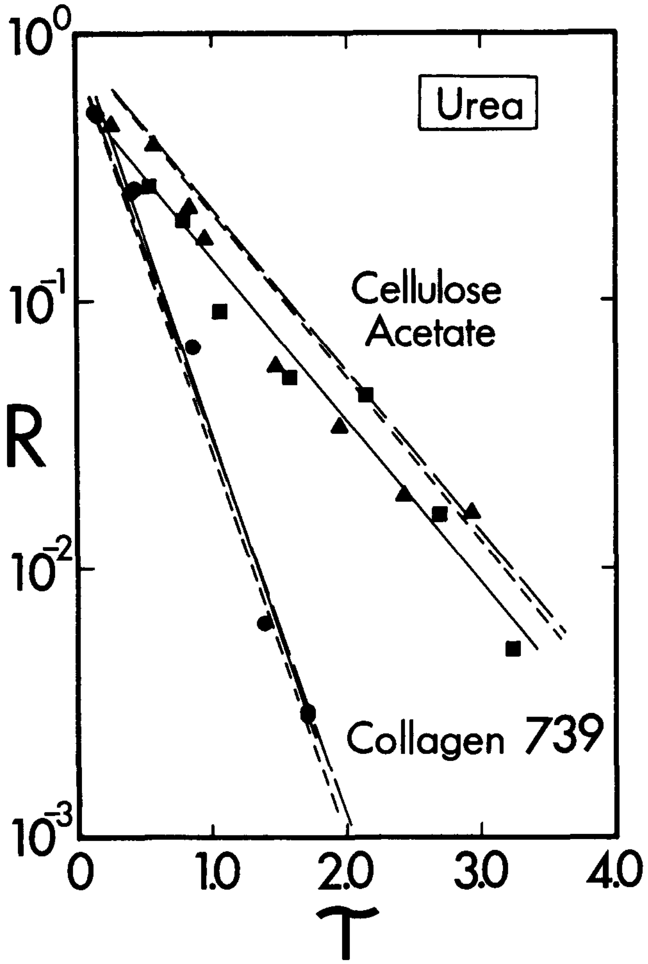

**Fig. 3. Logarithm of $R$ vs. $\tau$ for the diffusion of urea in collagen 739 and cellulose acetate tubular membranes. The solid lines are least-square fits of the data. The squares and triangles represent data for the cellulose acetate membranes taken on different days by different investigators. The dashed lines for collagen 739 were computed using the following values for membrane constants:**

$$K = 0.89,\ a/b = 0.75,\ D_2/D_1 = 2.1$$

$$Sh = \infty\ (- - -)\ \text{and}\ Sh = 100\ (\text{———})$$

**The dashed lines for cellulose acetate were computed using the following values:**

$$K = 0.66,\ a/b = 0.80,\ D_2/D_1 = 5.2$$

$$Sh = \infty\ (- - -)\ \text{and}\ Sh = 60\ (\text{———})$$

and $\epsilon = 0.85 \pm 0.02$ determined by Viswanadham and Kramer (1975). Because of the smallness of the membranes and the inaccessibility of the internal surface of the tubes, measurements of the equilibrium partition coefficient $K$ were not precise (Von Deak, 1975; Weinberg, 1974; and Dauber, 1973) and are not reported here.

Typical experimental measurements of R as a function of $\tau$ are shown in Figure 3 for the diffusion of urea and in Figure 4 for the diffusion of PEG in collagen and cellulose acetate membranes. The solid straight lines running through the data represent least-square fits of the experimental data. All of the data points were judged to be in the region where $\ln(R)$ varies linearly with $\tau$. The dashed lines in Figure 3 represent predicted values for the $\ln(R)$ vs. $\tau$ curve as explained in the section on validation experiments. The reproducibility of the data is indicated in Figure 3, where the squares and triangles represent data for the cellulose acetate membranes taken on different days by different investigators.

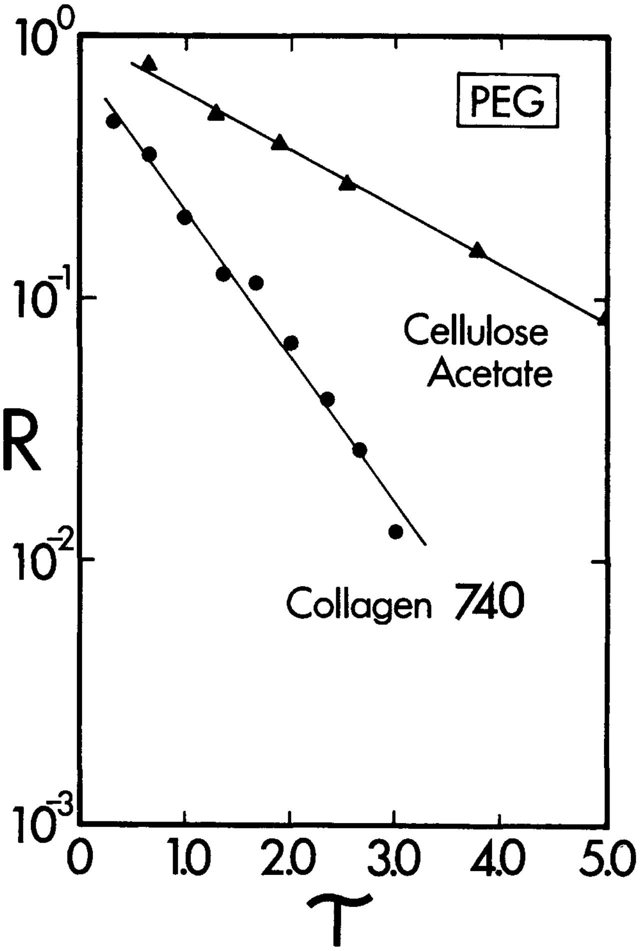

**Fig. 4. Logarithm of $R$ vs. $\tau$ for the diffusion of polyethylene glycol ($MW \sim 4\,000$) in collagen 740 and cellulose acetate tubular membranes.**

The experimental results obtained from an analysis of the ln $(R)$ vs. $\tau$ curves are summarized in Table 2. From this table it can be seen that for a given membrane, $D_{\text{eff}}/D_1$ decreases with increasing solute molecular weight. For a given solute, $D_{\text{eff}}$ for collagen is between 2.6 and 4 times $D_{\text{eff}}$ for cellulose acetate over the range of solutes studied. However, the permeabilities of the two membranes for a given solute are comparable because the tubular membranes made of collagen are much larger than those made of cellulose acetate. On the basis of the $D_{\text{eff}}/D_1$ data for the diffusion of urea in collagen membranes, there does not appear to be a significant difference between collagen prepared in lot HF-739 and lot HF-740. The reproducibility of the experimental data can be judged by comparing the results for the duplicate experiments with cellulose acetate membranes in Table 2. The 95% confidence limits (95% CL) were determined by the procedure described previously in the section on error analysis.

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## NOTATION

$a$ = inner radius of tubular membrane, cm

$b$ = outer radius of tubular membrane, cm

$C_1$ = concentration in the solutions external to the membrane, moles/liter of solution

$C_2$ = concentration in the membrane, moles/liter of wet membrane

$D_1$ = diffusivity in the solutions external to the membrane, cm$^2$/s

$D_2$ = diffusivity in the membrane (based on $C_2$), cm$^2$/s

$D_{eff}$ = $KD_2$, effective diffusivity in the membrane (based on $C_1$), cm$^2$/s

$J_\nu(z)$ = Bessel function of the first kind, of order $\nu$

$k_b$ = mass transfer coefficient at membrane-fluid interface, cm/s

$K$ = $C_2/C_1$, equilibrium partition coefficient

$L$ = length of tubular membrane, cm

$\dot{M}$ = solute flow rate, moles/s

$P$ = permeability for tubular membranes defined by Equation (3), cm/s

$P_s$ = membrane permeability for steady state diffusion, cm/s

$P_u$ = large $\tau$ asymptotic value of membrane permeability for unsteady state diffusion, cm/s

$R$ = fraction of solute remaining in sealed membrane tube

$Re$ = $2b\, v_\infty\, \rho/\mu$, Reynolds number

$Sc$ = $\mu/(\rho D_1)$ = Schmidt number

$Sh$ = $k_b\, 2b/D_1$, Sherwood number

$t$ = exposure time, s

$T$ = temperature, °C

$v_\infty$ = approach velocity, cm/s

### Greek Letters

$\alpha_1$ = square root of the absolute value of the slope of a $\ln(R)$ vs. $\tau$ graph in the region where $\ln(R)$ varies linearly with $\tau$

$\beta^2$ = $D_1/D_2$, ratio of diffusivities

$\epsilon$ = volume fraction water

$\kappa$ = $a/b$, ratio of inner radius to outer radius

$\mu$ = viscosity, poise

$\rho$ = density, g/cm$^3$

$\tau$ = $D_1 t/b^2$, dimensionless exposure time

### Superscripts

$\overline{X}$ = average value of $X$ for all tubular membranes used in a particular experiment

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