

DETERMINATION OF PORE RADIUS OF HOLLOW-FIBER DIALYSIS MEMBRANES USING TRITIUM-LABELED WATER

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Introduction

Current techniques of scanning electron microscopy are incapable of finding pores in dialysis membranes. Indirect methods of determining their pore size have been reported. Klein^{1,6)} proposed an excellent method using a well-known pore model, in which solute permeability is first measured with various solutes capable of penetrating dialysis membranes. Pure water and solute permeability data allow determination of pore radius depending on the solutes used. Values for pore radius are lower with ³H-water than with ¹⁴C-urea.

We have proposed a tortuous pore model improved from the pore model, with which structural parameters of pore radius, surface porosity and tortuosity may be determined for dialysis membranes from pure water and solute permeability and water content data. The structural parameters obtained with radioisotope-labeled urea, glucose and sucrose were almost the same for each membrane, as reported in our previous paper.³⁾

The objective of the present paper is to measure the solute permeability of commercially available dialysis membranes using ³H-water, followed by determination of structural parameters with the tortuous pore model, and to clarify the dependence of the parameters on the solutes used.

1. Tortuous Pore Model

Using the tortuous pore model, the solute and pure water permeability can be expressed by Eqs. (1) and (2):

$$P_m = Df(q)S_D(A_k/\tau/\Delta X) \quad (1)$$

$$L_w = (r_p^2/8\mu)(A_k/\tau/\Delta X) \quad (2)$$

From Eqs. (1) and (2),

$$P_m/L_w = Df(q)S_D(8\mu/r_p^2) \quad (3)$$

where

$$f(q) = (1 - 2.1q + 2.1q^3 - 1.7q^5 + 0.72q^6) / (1 - 0.76q^5) \quad (4)$$

$$S_D = (1 - q)^2 \quad (5)$$

$$q = r_s/r_p \quad (6)$$

which is exactly identical with the equation obtained by Klein.¹⁾ Equation (3) is strictly applicable only if the $(A_k/\tau/\Delta X)$ terms in Eqs. (1) and (2) are equal; this is true if P_m and L_w can be measured for the same solute.

Introduction of P_m and L_w data into Eq. (3) will yield the pore radius of the membranes tested by iteration. Values for $(A_k/\tau/\Delta X)$ can be calculated from the resulting pore radius by Eq. (2). The tortuosity can be expressed by Eq. (7):

$$\tau = H/A_k \quad (7)$$

Here τ and A_k can be obtained by Eqs. (8) and (9):

$$\tau = \{H/\Delta X/(A_k/\tau/\Delta X)\}^{1/2} \quad (8)$$

$$A_k = \{H\Delta X/(A_k/\tau/\Delta X)\}^{1/2} \quad (9)$$

2. Experimental

2.1 Dialysis membrane

Technical data on the commercially available dialysis membranes tested are summarized in **Table 1**. **Table 2** presents experimental values of the inner diameter and wall thickness of hollow-fiber dialysis membranes, expressed as the mean and standard deviation of 100 measurements under wet conditions.

2.2 Water content

The water content ($v/v\%$) of the membranes tested, which indicated the space required for solute transport, was measured by the standard method using 120 membrane tubes 5 cm in length.

2.3 Solute

Tritium-labeled water was used to determine solute permeability of dialysis membranes in the present

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Table 1. Technical data on hollow-fiber dialyzers and dialysis membranes

Dialyzer (Manufacturer)	Number of fibers*	Material	Surface area* [m ²]	Membrane*		
				Inner diameter [μm]	Wall thickness [μm]	Fiber length [mm]
MC 0.8H (Senko Medical)	6,600	Cuprophane	0.72	200	8	172
TAF 10 (Terumo)	6,850	Regenerated cellulose	1.02	200	12	237
AM-10 (Asahi Medical)	10,700	Regenerated cellulose	1.18	200	15	176
AM-2000U (Asahi Medical)	10,900	Regenerated cellulose	1.49	200	8	218
KF-101 (Kuraray)	7,800	Ethylenevinyl alcohol	1.21	200	32	246
KF-101C (Kuraray)	7,800	Ethylenevinyl alcohol	1.23	200	32	250
KPK-101 (Kuraray)	6,528	Ethylenevinyl alcohol	1.26	250	33	245
B2-100 (Toray Medical)	11,000	Polymethyl methacrylate	1.21	200	25	175

* Data taken from manufacturers' catalogues

Table 2. Water content, inner diameter, wall thickness, solute and pure water permeability data of hollow-fiber dialysis membranes

Dialyzer	Solute permeability [μm s ⁻¹]*		Pure water permeability L_p [m ³ m ⁻² Ts ⁻¹ Pa ⁻¹]***	Water content H [v/v%]****	Inner diameter***** [μm]	Wall thickness***** [μm]
	³ H-Water (20)	¹⁴ C-Urea (62)**				
MC 0.8H	34.3 ± 2.7 (5)	11.6 ± 3.7 (20)	11.1	66	212 ± 13	20.7 ± 2.8
TAF-10	24.1 ± 1.6 (5)	8.42 ± 0.23 (4)	11.2	61	203 ± 11	26.4 ± 2.9
AM-10	20.7 ± 1.5 (5)	7.83 ± 0.13 (15)	5.88	65	204 ± 22	30.7 ± 2.4
AM-2000U	31.5 ± 5.6 (5)	12.2 ± 1.1 (5)	15.8	61	200 ± 12	19.2 ± 2.2
KF-101	8.82 ± 0.77 (5)	3.52 ± 0.17 (11)	9.36	46	228 ± 14	41.1 ± 5.2
KF-101C	8.89 ± 0.75 (5)	4.02 ± 0.08 (10)	16.4	49	220 ± 10	44.3 ± 4.2
KPK-101	nil	5.23 ± 0.29 (7)	23.1	nil	251 ± 23	51.8 ± 5.2
B2-100	12.6 ± 1.8 (5)	6.51 (1)	6.38	54	202 ± 7	25.3 ± 2.4

* Data expressed in mean ± S.D. (N)

** Data obtained in our previous paper³⁾

*** Data measured at 310K

**** Data measured at room temperature

***** Data taken under wet conditions and expressed in mean ± S.D., $N = 100$

study. Values for diffusivity in free water and Stokes radius at 310 K are $2970 \mu\text{m}^2 \text{s}^{-1}$ and 0.107 nm for ^3H -water, and $1810 \mu\text{m}^2 \text{s}^{-1}$ and 0.182 nm for ^{14}C -urea, respectively.

2.4 Solute and pure water permeability

Dialysis experiments were made to determine solute permeability at a dialysate flow rate such that the boundary layer formed on the outside of hollow-fiber membranes could be completely eliminated. A membrane tube filled with ^3H -water solution of a concentration of 5 Ci m^{-3} was sealed at either end and fixed in the experimental apparatus for dialysis. The ^3H -water was dialyzed five or more times for predetermined periods at 310 K. Solute concentration in the membrane tube was measured with a liquid scintil-

lation counter (Aloka 900-LSC, Aloka, Tokyo) immediately after the dialysis experiments. Data analysis was based on the method of Stevenson.^{4,5)} With ^{14}C -urea, practically the same dialysis experiments were made for each membrane in the work reported in our previous paper.³⁾

The pure water permeability was measured with a dialyzer, which had been rinsed with 2 liters of saline to remove surface-active agents from membrane surfaces. Feed pressures at inlet P_{Bi} and at outlet P_{Bo} and filtrate pressure P_F were measured at a temperature of 310 K. The pure water permeability was calculated by Eqs. (10) and (11):

$$\Delta P = (P_{Bi} + P_{Bo})/2 - P_F \quad (10)$$

Table 3. Calculation of r_p , $(A_k/\tau/\Delta X)$, A_k and τ by tortuous pore model

Dialyzer	r_p [nm]		$(A_k/\tau/\Delta X)$ [mm ⁻¹]		A_k [%]*		τ [—]*	
	³ H-Water	¹⁴ C-Urea**	³ H-Water	¹⁴ C-Urea**	³ H-Water	¹⁴ C-Urea**	³ H-Water	¹⁴ C-Urea**
MC 0.8H	2.06	2.66	14.5	8.62	45	34	1.5	1.9
TAF-10	2.52	3.23	9.76	5.91	40	31	1.5	2.0
AM-10	1.91	2.30	8.92	6.12	42	35	1.5	1.9
AM-2000U	2.62	3.18	12.7	8.59	39	32	1.6	1.9
KF-101	3.94	4.75	3.34	2.29	25	21	1.8	2.2
KF-101C	5.31	6.03	3.26	2.53	27	23	1.8	2.1
KPK-101	nil	6.25	nil	3.26	nil	nil	nil	nil
B2-100	2.64	2.68	5.06	4.84	26	25	2.1	2.2

* Surface porosity A_k and tortuosity τ were calculated from the values for $(A_k/\tau/\Delta X)$ of ³H-water and ¹⁴C-urea.

** Data obtained in our previous paper³⁾

$$L_w = Q_F / (A \times \Delta P) \quad (11)$$

3. Results and Discussion

Experimental values of solute and pure water permeability of the dialysis membranes tested using ³H-water and ¹⁴C-urea are summarized in Table 2. Solute permeability depends on the wall thickness and water content of hollow-fiber dialysis membranes. Pure water permeability depends on the pore size, wall thickness and water content.

Calculated values of pore radius from solute and pure water permeability data obtained with ³H-water and ¹⁴C-urea differ for hydrophilic membranes but not for hydrophobic PMMA membranes (B2-100), and are lower with ³H-water than with ¹⁴C-urea, as listed in Table 3. The PMMA membranes may have no affinity for either urea or water, resulting in almost the same pore radius for each solute.

Table 3 also presents values for surface porosity and tortuosity obtained by using Eqs. (8) and (9). Surface porosity is higher and tortuosity is lower with ³H-water than with ¹⁴C-urea, and for cellulosic membranes than for synthetic polymer membranes. The solutes used give almost the same surface porosity and tortuosity for the PMMA membranes.

Intramembrane diffusivity D_m for each membrane can be determined by introducing $(A_k/\tau/\Delta X)$ of ³H-water and solute permeability data into Eq. (12).

$$D_m = P_m / (A_k/\tau/\Delta X) \quad (12)$$

The ratio of intramembrane diffusivity to diffusivity in free water for each membrane is summarized in Table 4. Much discrepancy is found between calculated and experimental values for D_m/D with ¹⁴C-urea except for PMMA membranes, because ¹⁴C-urea tends to adsorb slightly on cellulosic and ethylene vinylalcohol copolymer membranes with a hydrophilic property and differing paths of solute transport are present for ³H-water and ¹⁴C-urea. No tritium-labeled water tends to adsorb on the mem-

Table 4. Ratio of intramembrane diffusivity D_m to diffusivity in free water D

Dialyzer	D_m^*/D	
	³ H-Water (20)	¹⁴ C-Urea (62)
MC 0.8H	0.80 (0.80)**	0.44 (0.74)
TAF-10	0.83 (0.83)	0.48 (0.79)
AM-10	0.78 (0.78)	0.48 (0.71)
AM-2000U	0.84 (0.84)	0.53 (0.78)
KF-101	0.89 (0.89)	0.58 (0.85)
KF-101C	0.92 (0.92)	0.68 (0.88)
B2-100	0.84 (0.84)	0.65 (0.68)

* Intramembrane diffusivity may be represented by $D_m = P_m / (A_k/\tau/\Delta X)$, where the values obtained for $(A_k/\tau/\Delta X)$ of ³H-water by the tortuous pore model were used.

** According to the tortuous pore model, the ratio of intramembrane diffusivity to diffusivity in free water is theoretically represented by $D_m/D = f(q)S_p$. Parenthesized figures indicate theoretical values of D_m/D .

branes because of the previous formation of clusters of H₂O molecules on the pore walls. In the present study, we obtained higher values of pore radius and lower values of solute permeability for test solutes which tend to adsorb on the membrane tested, leading to lower values of surface porosity and higher values of tortuosity.

Much attention should be paid to choice of solutes in characterizing dialysis membranes from permeability data. Little adsorption is reported to occur on cellulosic membranes compared with synthetic polymer membranes.²⁾ Even slight affinity of test solute for membrane materials, however, affects permeability data, causing poor results for membrane characterization. The present method using tritium-labeled water is suitable for characterizing dialysis membranes since no adsorption of tritium-labeled water on fully wetted or hydrophobic membranes tends to occur and the same paths of solute transport are used in measuring solute and pure water per-

meability with tritium-labeled water and water.

Conclusions

1. Much attention should be paid to the affinity of test solute for membrane materials in characterizing dialysis membranes from permeability data.

2. Pore model studies on characterization of hydrophilic membranes for dialysis give lower values of pore radius and tortuosity, and higher values of surface porosity using ^3H -water than using ^{14}C -urea.

3. The method using ^3H -water is suitable for characterizing dialysis membranes because of lack of adsorption of ^3H -water on fully wetted or hydrophobic dialysis membranes and determination of P_m and L_w for the same solute.

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Nomenclature

A	= surface area	$[\text{m}^2]$
A_k	= fractional surface porosity	$[-]$
D	= diffusivity in free water	$[\text{m}^2 \cdot \text{s}^{-1}]$

D_m	= intramembrane diffusivity	$[\text{m}^2 \cdot \text{s}^{-1}]$
$f(q)$	= wall correction factor for diffusion	$[-]$
H	= fractional water content	$[-]$
L_w	= pure water permeability	$[\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}]$
ΔP	= transmembrane pressure	$[\text{Pa}]$
P_{Bi}	= feed pressure at inlet	$[\text{Pa}]$
P_{Bo}	= feed pressure at outlet	$[\text{Pa}]$
P_F	= filtrate pressure	$[\text{Pa}]$
P_m	= solute permeability	$[\text{m} \cdot \text{s}^{-1}]$
q	= r_s/r_p	$[-]$
Q_F	= filtrate flow rate	$[\text{m}^3 \cdot \text{s}^{-1}]$
r_p	= radius of membrane pore	$[\text{m}]$
r_s	= Stokes radius of solute	$[\text{m}]$
S_D	= steric hindrance factor for diffusion	$[-]$
ΔX	= membrane thickness	$[\text{m}]$
μ	= viscosity	$[\text{Pa} \cdot \text{s}]$
τ	= tortuosity	$[-]$

Literature Cited

- 1) Klein, E., F. F. Holland and K. Eberle: *J. Membrane Sci.*, **5**, 173 (1979).
- 2) Matthiasson, E. and B. Sivik: *Desalination*, **35**, 59 (1980).
- 3) Sakai, K., S. Takesawa, R. Mimura and H. Ohashi: *J. Chem. Eng. Japan.*, **20**, 351 (1987).
- 4) Stevenson J. F.: *Am. Inst. Chem. Eng. J.*, **20**, 461 (1974).
- 5) Stevenson J. F.: *Am. Inst. Chem. Eng. J.*, **21**, 1192 (1975).
- 6) Wendt, R. P., E. Klein, E. H. Bresler, F. F. Holland, R. M. Serino and H. Villa: *J. Membrane Sci.*, **5**, 23 (1979).

PRESSURE DETERMINATION OF VAPOR-LIQUID EQUILIBRIUM USING SUCCESSIVE SUBSTITUTION METHOD

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Introduction

Successive substitution is the most popular method for solving the simultaneous nonlinear equations of vapor-liquid equilibrium due to its simplicity, even though the Newton-Raphson method can also be used.

Heidemann³⁾ reviewed the successive substitution method used in high-pressure phase equilibrium calculation. Veeranna and Rihani⁸⁾ showed that poor initial pressure or temperature guesses can lead to a trivial solution and recommended an initial pres-

sure or temperature correlation for bubble or dew points of various mixtures.

Precise details are lacking in the open literature on algorithms to carry out these calculations. This paper concerns an iteration formula for the pressure determination of vapor-liquid equilibrium. Among the publications which deal with the computational procedures, Hanley and Rosen²⁾ presented the following formula:

$$P^{(k+1)} = P^{(k)} \left/ \sum_{i=1}^N y_i / K_i^{(k)} \right. \quad (1)$$

Similarly, for a bubble-point pressure,

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