

# Size of Polymeric Particles Forming Hemodialysis Membranes Determined from Water and Solute Permeabilities

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**ABSTRACT:** Regarding hemodialysis membranes as layers packed with uniform polymeric particles, the size of the particles is determined using the Kozeny–Carman equation. Diameter of the spheres forming cellulosic membranes is the same order as the size of primary polymeric particles determined by electron microscopy in a previous article. Pore radii of the membranes calculated by the Kozeny–Carman equation are in agreement with those determined by the tortuous capillary pore model. The result suggests that an estimate of a pore radius of a membrane is feasible by the Kozeny–Carman equation only with water permeability of the membrane. Intramembrane diffusion coefficients of vitamin B<sub>12</sub> calculated from an equation derived from the analogy of heat conduction in heterogeneous media consisting of a continuous phase and particles are larger than the experimental values. The result suggests the failure of the analogy between heat conduction and diffusion of vitamin B<sub>12</sub> in a heterogeneous medium. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 833–840, 1998

**Key words:** hemodialysis membrane; Kozeny–Carman equation; tortuous capillary pore model; packed layer; heterogeneous media

## INTRODUCTION

Schultz and Asunmaa<sup>1</sup> have observed the structure of skin layers of cellulose acetate membranes for reverse osmosis by electron microscopy in 1966 and have determined the pore diameters by the observation and the measurements of water permeability of the membranes, assuming that the membranes consist of uniform spheres. However, structure of hemodialysis membranes of which water permeability is almost the same as that of reverse osmosis has not yet been identified in

spite of further remarkable improvement in electron microscopy.

Sakai et al.<sup>2</sup> have presented the structure of hemodialysis membranes determined by the tortuous capillary pore model assuming that uniform tortuous capillary pores exist in the membranes and that solute and water permeate only through the pores.

Because the structure of a hemodialysis membrane is generally formed by the microphase separation of a polymer–solvent system, the membranes are considered to consist of polymeric aggregations, which may be lamellas or micelles in crystalline polymers, such as cellulose. Consequently, it is reasonable to assume that a hemodialysis membrane consists of polymeric particles.

In this article, the authors regard hemodialysis

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membranes as heterogeneous media consisting of water and uniform polymeric particles where any solutes or water are incapable of permeating.

First, we calculate equivalent pore radii from water content and water permeability of the membranes using the Kozeny–Carman equation<sup>3,4</sup> and then compare them with those determined by the tortuous capillary pore model.

Next, we apply an equation for diffusion in heterogeneous media derived by Crank<sup>5</sup> to permeation of vitamin B<sub>12</sub> through the membranes and discuss the membrane structures formed by polymeric particles.

## THEORY

### Water Permeability of a Packed Layer

Water permeability  $L_P$  (m Pa<sup>-1</sup> s<sup>-1</sup>) of a packed layer is given by the so-called Kozeny–Carman equation,<sup>3</sup>

$$L_P = \frac{\varepsilon^3}{5\mu(1 - \varepsilon^2)S_V^2\Delta\chi} \quad (1)$$

where  $\varepsilon$  (—) and  $\Delta\chi$  (m) denote porosity and thickness of the layer, respectively;  $\mu$  (Pa s), the viscosity of water; and  $S_V$  (m<sup>-1</sup>), the specific surface of the particles packed in the layer.

Assuming that the packed layer is equivalent to a bundle of uniform circular capillaries, the equivalent radius of the capillaries,  $r_e$  (m), is obtainable from

$$r_e = 2m = (20\eta\Delta\chi L_P/\varepsilon)^{0.5} \quad (2)$$

where  $m$  denotes the hydraulic radius (m).<sup>4</sup>

### Diffusion Coefficient of a Solute in a Heterogeneous Medium

Crank<sup>5</sup> has presented the following equation by the analogy of an expression concerning the electric conductivity and capacity of disperse systems presented by Fricke,<sup>6</sup> giving overall diffusion coefficient  $D$  (m<sup>2</sup>/s) of a solute in a heterogeneous medium in which particles with diffusion coefficient  $D_a$  (m<sup>2</sup>/s) of the solute are dispersed in a continuous phase with diffusion coefficient  $D_b$  (m<sup>2</sup>/s) of the solute,

$$\frac{D - D_b}{D + \chi D_b} = \nu_a \frac{D_a - D_b}{D_a + \chi D_b} \quad (3)$$

where  $\nu_a$  (—) denotes volume fraction of the dispersed phase. A value of  $\chi$  (—) is called the “shape factor” and satisfies the following equation for any heterogeneous media with particles of various shapes in sphere, cylinder, parallelepiped, disk, or cube<sup>7</sup> as

$$\chi = 3/\psi - 1 \quad (4)$$

where  $\psi$  (—) is the sphericity of the particle defined as follows:

$$\psi = A_s/A_p \quad (5)$$

where  $A_s$  (m<sup>2</sup>) is the surface area of the sphere with volume equal to that of the particle, and  $A_p$  (m<sup>2</sup>) is the surface area of the particle.

## EXPERIMENTAL

### Technical Data on Hemodialysis Membranes

Table I summarizes the technical data, including water content  $H$  and volume fraction of freezable water ( $H_f + H_{fb}$ ) in the membranes measured by differential scanning calorimetry (DSC).<sup>8</sup>

### Determination of Membrane Structure by the Tortuous Capillary Pore Model

The structural parameters of the hemodialysis membranes, namely, pore radius, fractional surface porosity, and tortuosity, were determined by the tortuous capillary pore model<sup>2</sup> from permeability of tritium-labeled water (HTO) measured by the previous method,<sup>10</sup> water content, and water permeability listed in Table I.

### Intramembrane Diffusion Coefficient of Vitamin B<sub>12</sub>

Intramembrane diffusion coefficients of vitamin B<sub>12</sub> (VB<sub>12</sub>) for the hemodialysis membranes were measured by the optical method presented by Kanamori et al.<sup>11</sup> The method enables measurement of solute permeability of a single hollow-fiber membrane without the influence of flow conditions inside and around the membrane.

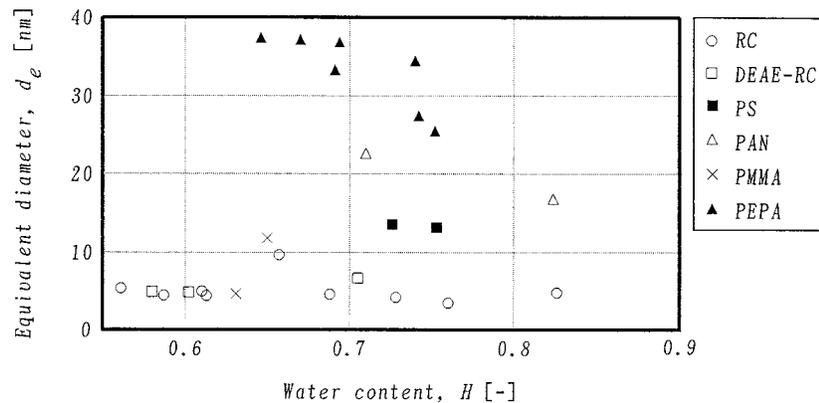
**Table I** Technical Data on Hemodialysis Membranes

Type	Manufacturer or Representative	Material (Abbreviation)	ID ( $\mu\text{m}$ )	$\Delta x$ ( $\mu\text{m}$ )	$L_p$ ( $\text{mL m}^{-2} \text{h}^{-1} \text{mmHg}^{-1}$ )	H (—)	$H_f + H_{fb}$ (—)
AM-SD-M	Asahi Medical	Regenerated cellulose (RC)	188 ± 15 (100)	23.7 ± 3.0 (200)	3.8	0.587	0.345
AM-NeoUP	Asahi Medical	Regenerated cellulose (RC)	209 ± 12 (100)	27.5 ± 3.6 (200)	13.0	0.760	0.511
AM-UP	Asahi Medical	Regenerated cellulose (RC)	204 ± 7 (100)	30.3 ± 1.6 (200)	8.8	0.688	0.439
AM-FP	Asahi Medical	Regenerated cellulose (RC)	195 ± 9 (100)	30.5 ± 3.6 (200)	11.6	0.728	0.525
AM-EP	Asahi Medical	Regenerated cellulose (RC)	179 ± 13 (100)	30.2 ± 3.5 (200)	54.2	0.826	0.663
F1	Akzo Novel	Cuprophane <sup>R</sup> (RC)	212 ± 18 (100)	24 ± 1 (200)	4.2	0.561	0.351
B1	Akzo Novel	Cuprophane <sup>R</sup> (RC)	211 ± 20 (100)	22 ± 1 (200)	5.2	0.613	0.372
RC-HP400	Akzo Novel	Cuprophane <sup>R</sup> (RC)	214 ± 20 (100)	35 ± 2 (200)	24.6	0.657	0.413
MC55	Akzo Novel	Hemophan <sup>R</sup> (DEAE-RC)	212 ± 15 (100)	24 ± 1 (200)	4.2	0.580	0.340
MC65	Akzo Novel	Hemophan <sup>R</sup> (DEAE-RC)	211 ± 15 (100)	22 ± 3 (200)	5.6	0.602	0.361
MC-HP200	Akzo Novel	Hemophan <sup>R</sup> (DEAE-RC)	218 ± 20 (100)	38 ± 3 (200)	17.9	0.705	0.459
TAF(W)	Terumo	Regenerated cellulose (RC)	203 ± 11 (100)	26.4 ± 2.9 (200)	5.4	0.610	0.406
FB-UGA	Toyobo	Cellulose triacetate (CTA)	201 ± 8 (100)	12.4 ± 2.0 (200)	62.4	0.858	0.772
F	Fresenius	Polysulfone (PS)	189 ± 21 (100)	49.0 ± 7.2 (200)	73.5	0.726	
PS-UW	Kawasumi Laboratories	Polysulfone (PS)	201 ± 6 (100)	48.3 ± 3.5 (200)	96.6	0.753	0.781
PAN-CX <sub>2</sub>	Asahi Medical	Polyacrylonitrile (PAN)	248 ± 10 (100)	64.9 ± 8.2 (200)	301.1	0.824	0.794
PAN-DX	Asahi Medical	Polyacrylonitrile (PAN)	245 ± 15 (100)	30.0 ± 4.0 (200)	277.4	0.710	0.702
BK-P	Toray	Poly(methyl methacrylate) (PMMA)	189 ± 12 (100)	32.3 ± 3.3 (200)	36.9	0.650	0.542
B2-H	Toray	Poly(methyl methacrylate) (PMMA)	195 ± 8 (100)	20.9 ± 2.6 (200)	7.2	0.631	
FLX-GW	Nikkiso	Polyether polymer alloy (PEPA) <sup>b</sup>	206 ± 13 (100)	32.0 ± 2.8 (200)	536.2	0.752	0.733
1.0-a <sup>a</sup>	Nikkiso	Polyether polymer alloy (PEPA) <sup>b</sup>	185 ± 6 (100)	37.1 ± 3.0 (200)	310.0	0.646	0.639
1.0-b <sup>a</sup>	Nikkiso	Polyether polymer alloy (PEPA) <sup>b</sup>	184 ± 5 (100)	37.3 ± 3.2 (200)	391.3	0.670	0.660
1.0-c <sup>a</sup>	Nikkiso	Polyether polymer alloy (PEPA) <sup>b</sup>	183 ± 3 (100)	37.3 ± 3.5 (200)	472.8	0.742	0.724
1.0-d <sup>a</sup>	Nikkiso	Polyether polymer alloy (PEPA) <sup>b</sup>	185 ± 6 (100)	37.0 ± 2.8 (200)	396.3	0.691	0.679
1.5-c <sup>a</sup>	Nikkiso	Polyether polymer alloy (PEPA) <sup>b</sup>	184 ± 5 (100)	37.3 ± 2.9 (200)	496.2	0.694	0.681
2.0-c <sup>a</sup>	Nikkiso	Polyether polymer alloy (PEPA) <sup>b</sup>	184 ± 5 (200)	37.5 ± 3.1 (200)	726.7	0.740	0.722

ID is the inner diameter of hollow fibers;  $\Delta x$ , member thickness;  $L_p$ , pure water permeability;  $H$ , water content measured by the ordinary method;<sup>8</sup>  $H_f + H_{fb}$ , volume fraction of freezable water in a membrane.<sup>8</sup> Data expressed in mean ± standard deviation. Values in parentheses are numbers of data.

<sup>a</sup> Trial products. Numeric values and letters in the types indicate the polyarylate-polyethersulfone blend ratios and the core fluid compositions in the spinning process, respectively.<sup>9</sup>

<sup>b</sup> Shimizu et al.<sup>9</sup>



**Figure 1** Equivalent diameter of polymeric spheres forming dialysis membranes of various materials calculated from water content with the Kozeny–Carman equation.

## RESULTS AND DISCUSSION

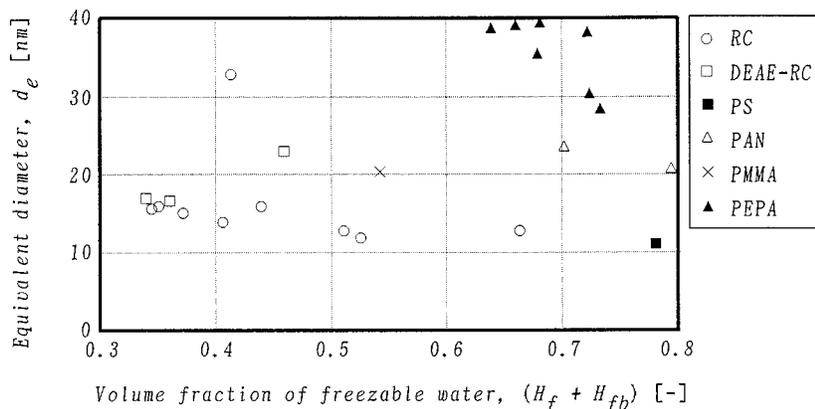
### Diameter of Particles Forming Hemodialysis Membranes Calculated from Water Permeability

Regarding a hemodialysis membrane as a packed layer consisting of uniform polymeric particles, specific surface of the particles  $S_V$  is obtainable from eq. (1) with the data in Table I. In the present study, the water content  $H$  or volume fraction of freezable water ( $H_f + H_{fb}$ ) was considered to be equal to porosity  $\varepsilon$  in eq. (1). Equivalent diameter  $d_e$  (m) of a sphere of volume equal to that of the particle is calculated from  $S_V$  because  $S_V$  is  $6/d_e$  for the sphere.

Figures 1 and 2 show  $d_e$  plotted against  $H$  and ( $H_f + H_{fb}$ ), respectively. The values of  $d_e$  were

nearly constant for each material of the membranes. Because the structures of the hemodialysis membranes shown in Table I are formed by the microphase separation of each polymer–solvent system, the diameters of the polymeric particles forming the membranes are considered to depend on each material of the membranes. The result supports the validity of regarding a hemodialysis membrane as a packed layer consisting of particles, as Schultz and Asunmaa<sup>1</sup> have presented.

Many researches on cellulose and its derivatives have been carried out, revealing their ultrastructure. Kamide and Manabe<sup>12</sup> observed the microphase separation of cuprammonium cellulose by electron microscopy and have reported that the structure formation of cuprammonium–cellulose membranes consists of the following two steps:



**Figure 2** Equivalent diameter of polymeric spheres forming dialysis membranes of various materials calculated from the volume fraction of freezable water with the Kozeny–Carman equation.

**Table II Permeability of Tritium-Labeled Water (HTO) and Structural Parameters of Hemodialysis Membranes**

Type	HTO Permeability ( $\mu\text{m/s}$ )	Pore Radius (nm)	Surface Porosity (—)	Tortuosity (—)
AM-SD-M	21.2	2.2	0.349	1.68
AM-NeoUP	22.8	4.2	0.423	1.80
AM-UP	24.5	3.3	0.444	1.55
AM-FP	26.7	3.6	0.475	1.53
AM-EP	33.1	7.2	0.544	1.52
F1	24.8	2.2	0.373	1.51
B1	24.9	2.4	0.369	1.66
RC-HP400	25.6	5.5	0.464	1.42
MC55	26.3	2.1	0.391	1.48
MC65	21.1	2.8	0.333	1.81
MC-HP200	31.0	4.2	0.558	1.26
FB-UGA	26.4	8.6	0.310	1.80
PS-UW	29.1	9.1	0.616	1.22
PAN-CX <sub>2</sub>	27.3	19.2	0.709	1.16
PAN-DX	28.7	17.9	0.459	1.55

precipitation of primary particles from 10 to 30 nm in diameter, and formation of secondary particles from 50 to 300 nm in diameter by collision with the primary particles.

The values of  $d_e$  calculated from  $H$  for the cellulosic membranes are considered to be unreasonable because the values are of the order of the size of the unit cell of cellulose.<sup>13</sup> However, Figure 2 provides the suitable values of  $d_e$  corresponding to the primary particle. The result suggests that volume fraction of freezable water ( $H_f + H_{fb}$ ) in a membrane is suited for the porosity related to water permeation through the membrane.

#### Comparison of Pore Radius Calculated by the Kozeny–Carman Equation from Water Permeability with That Determined by the Tortuous Capillary Pore Model

Table II summarizes HTO permeability and structural parameters of the hemodialysis membranes determined with the tortuous capillary pore model.<sup>2</sup> In Figure 3, the pore radii in Table II,  $r_p$ , are compared with those calculated by eq. (2) from the water permeabilities of the membranes,  $r_e$ .

The liner relation between  $r_p$  and  $r_e$  is observed, regardless of there being a deference in determining tortuosities between these two methods. Carman derived eq. (2) on the assumption of

$$\tau = (5/k_o)^{0.5} \quad (6)$$

where  $k_o$  varies between 2.0 and 2.5 according to the shape of cross section of capillary pores, giving the values of  $\tau$  from 1.44 to 1.58. On the other hand, the tortuous capillary pore model gives individual tortuosities to each membrane.

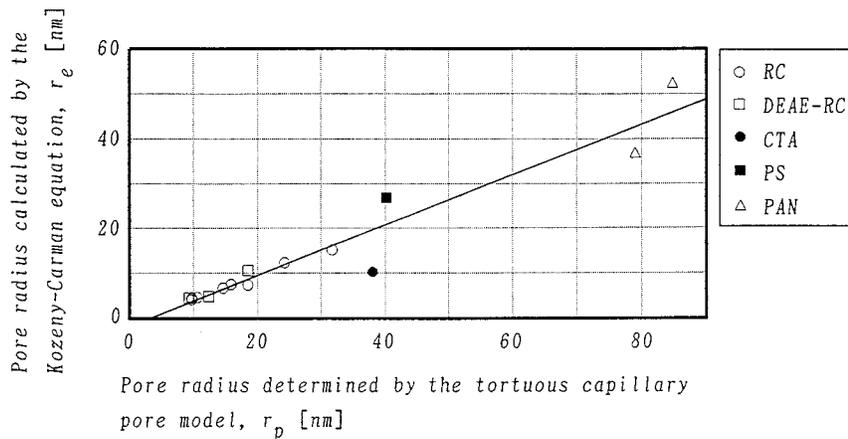
The tortuous capillary pore model needs not only water permeability but also permeability of tritium-labeled water, of which measurement is troublesome. However, Figure 3 suggests that an estimate of a pore radius is feasible by the Kozeny–Carman equation only with water permeability.

#### Intramembrane Diffusion Coefficient of Hemodialysis Membranes As Heterogeneous Media

Regarding a hemodialysis membrane as a heterogeneous medium consisting of water and uniform polymeric particles, where either any solute or water is incapable of permeating,  $D$  corresponds to intramembrane diffusion coefficient,  $D_a$  vanishes,  $D_b$  is considered to be equal to diffusion coefficient in free water, and  $\nu_a$  is equal to one minus water content  $H$  in eq. (3), leading to the following equation with eq. (4).

$$\psi = -3 \frac{D - D_b + \nu_a D_b}{(1 - \nu_a)(D - D_b)} \quad (7)$$

Values of  $\psi$  for the membranes listed in Table I were calculated from eq. (7) with the intramembrane coefficients of VB<sub>12</sub> and the water contents.



**Figure 3** Comparison of pore radius calculated by the Kozeny-Carman equation from water permeability with that determined by the tortuous capillary pore model.

The diffusion coefficient of  $VB_{12}$  in free water  $D_o$  is  $411 \mu\text{m}^2/\text{s}$  of the average of two values in previous articles.<sup>14,15</sup>

Table III summarizes the intramembrane diffusion coefficients of  $VB_{12}$  and  $\psi$ . The definition of the sphericity provides the maximal value of  $\psi$  as one, but all the values of  $\psi$  determined for the membranes are much larger than one. The result suggests that intramembrane diffusion coefficient in a hemodialysis membrane is smaller than overall diffusion coefficient in a layer consisting of water and particles, where either any solute or water is incapable of permeating and of which volume fraction in the layer is  $(1 - H)$ .

Two reasons for the conflict are considered, as follows: (1) the actual volume fraction of the particles is larger than  $(1 - H)$ , and (2) the diffusion coefficient in the continuous phase  $D_b$  is smaller than that in free water.

On the basis of the first supposition, volume fraction of freezable water in the membranes ( $H_f + H_{fb}$ ) was used instead of  $H$ , and the sphericities  $\psi'$  (—) were calculated as shown in Table III. Because freezable water is considered to consist of molecules having the same mobility as that of free water molecules and those having somewhat reduced mobility by polymer chains in a membrane,<sup>8</sup> the values of  $(H_f + H_{fb})$  were smaller than  $H$ . However,  $\psi'$  was also larger than one.

Next, diffusion coefficients of the continuous phases in the membranes  $D_b$  were calculated from eq. (3) at a sphericity of 1.0, where the intramembrane diffusion coefficient came to the minimum and at  $\nu_a = \{1 - (H_f + H_{fb})\}$ . The ratios of  $D_b$  to diffusion coefficient in free water  $D_o$  were plotted against  $(H_f + H_{fb})$  in Figure 4. Reduction in  $D_b$

compared with  $D_o$  may be caused by a decrease in molecular mobility in the membranes because the free volume relating to diffusion in water contained in the membranes is less than that in free water. However, that the values of  $D_b/D_o$  are not constant for each material is against the prerequisite to the derivation of eq. (3) that the diffusion coefficient in a continuous phase  $D_b$  is due to the material of the phase, which, in the present case, is water contained in the membranes.

It is well known that the ratio of intramembrane diffusion coefficient to diffusion coefficient in free water for a solute decreases with increasing molecular weight of the solute, but eq. (3) is incapable of interpreting this phenomenon. Equation (3) was derived from the analogy of heat conduction in heterogeneous media consisting of a continuous phase and particles of various shapes. The present result suggests the failure of the analogy between heat conduction and diffusion of  $VB_{12}$  in a heterogeneous medium.

## CONCLUSION

Assuming that a hemodialysis membrane consists of uniform polymeric particles, water and solute permeabilities of the membrane were discussed. The diameter of the spheres forming cellulosic membranes calculated from water permeability using the Kozeny-Carman equation is of the same order as that of the primary polymeric particles determined by electron microscopy in a previous article.

Pore radii of the membranes calculated by the Kozeny-Carman equation are in agreement with

**Table III Intramembrane Diffusion Coefficients of Vitamin B<sub>12</sub> and Sphericities of Polymeric Spheres of Hemodialysis Membranes**

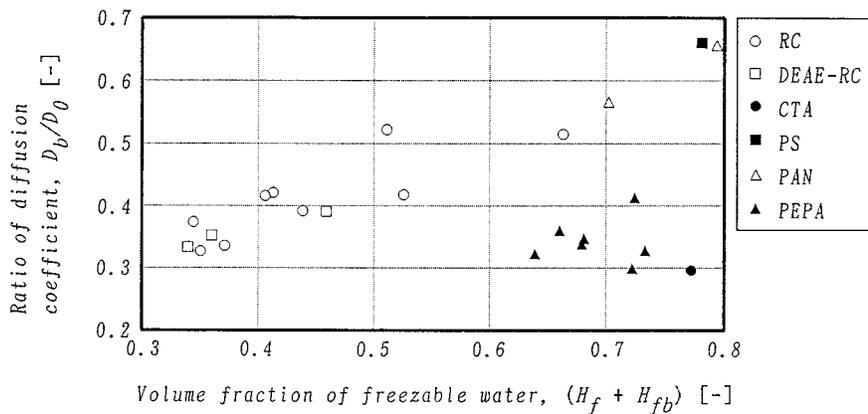
Type	Intramembrane Diffusion Coefficient of Vitamin B <sub>12</sub> (μm <sup>2</sup> /s)	Sphericity of Polymeric Spheres (—)	
		Ψ <sup>a</sup>	Ψ' <sup>b</sup>
AM-SD-M	39.9	2.77	2.39
AM-NeoUP	88.0	2.74	2.22
AM-UP	55.3	2.79	2.40
AM-FP	73.0	2.76	2.41
AM-EP	120	2.74	2.37
F1	35.6	2.78	2.47
B1	39.0	2.80	2.47
RC-HP400	55.4	2.76	2.34
MC55	35.0	2.80	2.46
MC65	39.6	2.79	2.43
MC-HP200	58.1	2.79	2.42
TAF(W)	53.6	2.71	2.34
FB-UGA	84.5	2.87	2.77
PS-UW	191	2.15	2.27
PAN-CX <sub>2</sub>	194	2.43	2.30
PAN-DX	142	2.35	2.33
FLX-GW	87.2	2.73	2.71
1.0-a	71.9	2.65	2.64
1.0-b	83.5	2.62	2.61
1.0-c	108	2.63	2.59
1.0-d	81.3	2.67	2.65
1.5-c	83.9	2.66	2.64
2.0-c	78.0	2.75	2.73

<sup>a</sup> Data calculated from water content *H*.

<sup>b</sup> Data calculated from volume fraction of freezable water (*H<sub>f</sub>* + *H<sub>fb</sub>*).

those determined by the tortuous capillary pore model. The result suggests that an estimate of a pore radius is feasible by the Kozeny–Carman equation only with water permeability.

Intramembrane diffusion coefficients of vitamin B<sub>12</sub> calculated by an equation derived for heat conduction in heterogeneous media are larger than all the experimental values. The result sug-



**Figure 4** Ratio of diffusion coefficient of vitamin B<sub>12</sub> in water contained in membranes to that in free water.

gests the failure of the analogy between heat conduction and diffusion of vitamin B<sub>12</sub> in a heterogeneous medium.

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## NOMENCLATURE

$A_s$	surface area of a sphere with a volume equal to that of a particle (m <sup>2</sup> )
$A_p$	surface area of a particle (m <sup>2</sup> )
$d_e$	equivalent diameter of polymeric spheres (m)
$D$	overall diffusion coefficient of a solute in a heterogeneous medium (m <sup>2</sup> /s)
$D_a$	diffusion coefficient of a solute in particles (m <sup>2</sup> /s)
$D_b$	diffusion coefficient of a solute in a continuous phase (m <sup>2</sup> /s)
$H$	water content (—)
$H_f$	volume fraction of free water (—)
$H_{fb}$	volume fraction of water of which molecular mobility is restricted by polymer chains (—)
$L_p$	water permeability (m Pa <sup>-1</sup> s <sup>-1</sup> )
$m$	hydraulic radius (m)
$r_e$	radius of a capillary pore determined by the tortuous capillary pore model (m)
$r_p$	radius of a capillary pore calculated by eq. (2) from water permeability (m) "shape factor" defined by eq. (3) (—)

$\nu_a$	volume fraction of dispersed phase (—)
$\tau$	tortuosity of a capillary pore (—)
$\psi$	sphericity defined by eq. (5) (—)

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