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Membrane Potential and Permeability Coefficient of Cellulose Membrane dyed with Congo Red[1]

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Visking cellulose tubing was dyed with various concentrations of Congo Red in order to change the charge density of the membrane. Sodium chloride solutions of different concentrations were placed in the two chambers of a cell divided by the membrane, and the membrane potential and the membrane permeability coefficient were measured at 34°C. The results obtained were analyzed on the of basis theoretical equations for membrane potential and membrane permeability coefficient derived on the basis of nonequilibrium thermodynamics. As the charge density of the membrane increased with the amount of Congo Red in the membrane (mol/cm^3), Congo Red adsorbed on the membrane partly dissociates, into a cation which enters the aqueous solution and a residual anion which remains on the membrane. From measurements of the porosity of the membrane, it was concluded that bound water in the membrane was displaced by Congo Red.

Keywords——Visking cellulose tubing; Congo Red; membrane potential; membrane permeability coefficient; charge density; porosity

Visking cellulose membrane was dyed with various amounts of Congo Red in order to change the charge density of the membrane. Then, the membrane potential and membrane permeability coefficient of these membranes were measured in aqueous sodium chloride and the porosities of the dyed membranes were studied by analyzing the experimental results according to theoretical equations for membrane potential and membrane permeability coefficient derived on the basis of nonequilibrium thermodynamics.[2]

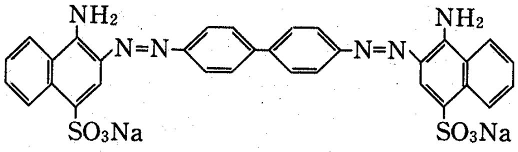

Chart 1

Theoretical

Consider a system, in which solutions of the same electrolyte at different concentrations are separated by a charged membrane and no volume flow is expected between the solutions. The concentrations of the solutions on both sides of the membrane are set to be $C^{\mathrm{I}}(=rC)$ and $C^{\mathrm{II}}(=C)$. Considering that the Donnan equillibrium exists between the membrane surface and the solution in contact with the surface, the concentrations of cations $C_+^{\mathrm{I}*}$ $C_+^{\mathrm{II}*}$ and anions C_-^{I}, $C_-^{\mathrm{II}*}$ on both membrane surfaces can be calculated.

The membrane potential arising here, which is the sum of Donnan potential and diffusion potential, in the case of a I-I valence electrolyte can be represented by eq. (1).[2,3]

$$\Delta E = E^{\mathrm{I}} - E^{\mathrm{II}} = \frac{RT}{F}\left\{-\ln r + \ln\frac{C_+{}^{\mathrm{I}*}}{C_+{}^{\mathrm{II}*}} + (2t_-^* - 1)\ln\frac{C_+{}^{\mathrm{I}*} + t_-^*\theta^*}{C_+{}^{\mathrm{II}*} + t_-^*\theta^*}\right\} \qquad (1)$$

E^{I} and E^{II} are potentials of solutions I and II, respectively, θ^* is the membrane charge density (mol/l), t_-^* the transport number of anion in the membrane, and r the concentration ratio of solutions I and II which is 2 in the present experiment. $C_+^{\mathrm{I}*}$ is calculated as follows in the case of a I-I valence electrolyte based on the assumption of Donnan equilibrium[2,3]

$$C_+{}^{\mathrm{I}*} = \frac{-\theta^* + \sqrt{\theta^* + 4\,(rC)^2}}{2} \qquad (2)$$

$C_-{}^*$ can easily be calculated from the condition of electroneutrality, eq. (3) and eq. (2)

$$C_-{}^{\mathrm{I}*} = C_+{}^{\mathrm{I}*} + \theta^* \qquad (3)$$

$C_+{}^{\mathrm{II}*}$ and $C_-{}^{\mathrm{II}*}$ can be calculated by setting $r=1$ in eqs. (2) and (3) for $C_+{}^{\mathrm{I}*}$ and $C_-{}^{\mathrm{I}*}$. In a sufficiently high concentration of the solution $C \gg |\theta^*|$, eq. (1) leads to the following equation:

$$\frac{F}{RT}\,\varDelta E = (2t_-{}^* - 1)\ln r + \frac{2\,(r-1)}{r}\,t_-{}^*\,(1-t_-{}^*)\,(\frac{\theta^*}{C}) \qquad (4)$$

Accordingly, $t_-{}^*$ can be calculated by plotting the measured values of the membrane potential $\varDelta E$ at high concentration against $(1/C)$ and extrapolating the plot to zero value of $(1/C)$. The reduced permeability coefficient of the membrane, Pr, is given by the following equation:[2)]

$$Pr = \frac{P}{P_\infty} = \frac{1}{C\,(r-1)}\,(C_+{}^{\mathrm{I}*} - C_+{}^{\mathrm{II}*}) - \frac{\theta^*}{2}\,(2t_-{}^* - 1)\ln\frac{C_+{}^* - t_-{}^*\theta}{C_+{}^{\mathrm{II}*} - t_-{}^*\theta} \qquad (5)$$

where P is the membrane permeability coefficient and P_∞ is the value at sufficiently high concentration. The experimental value of P is obtained from following equation:

$$J = P(r-1)/L \qquad (6)$$

where J is the amount of the solute which passes across unit area of the membrane in unit time, that is, the flux of the solution, and L is the thickness of the membrane. The membrane permeability coefficient P can be represented as follows;[4)]

$$P = fb\varphi D_0 \qquad (7)$$

where f is the membrane constant, b the distribution coefficient between the solution and the membrane surface, and D_0 the diffusion coefficient in water, φ being (D^*/D_0) when the diffusion coefficient in the membrane is D^*. In the case of the permeability of an electrolyte through a charged membrane, in which the distribution coefficient b is determined by Donnan equilibrium as described earlier, the value of b varies with the concentration of the electrolyte. The concentration dependence of the membrane permeability coefficient P is, therefore, considered to be ascribed primarily to that of the distribution coefficient b.

The porosity ε is the proportion of volume of vacant space in the membrane to the volume of the membrane,

$$\varepsilon = \frac{V_P}{V} \qquad (8)$$

where V and V_P are the volume of membrane and the volume of poies vacant space in the membrane, respectively. Using ε, the charge density θ^* is presented by the following equation.[4)]

$$\theta^* = \frac{1000\,Q}{F\varepsilon} \qquad (9)$$

where Q is the membrane charge per unit volume of the membrane and F is the Faraday constant.

Results and Discussion

The membrane potential was measured at 34°C by inserting silver-silver chloride electrodes directly into the respective solutions (Fig. 1). Since the potential difference obtained here

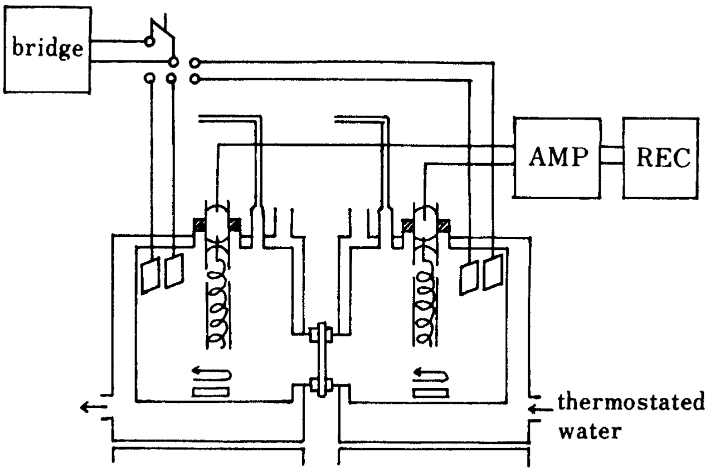

Fig. 1. Apparatus for the Measurement of Membrane Potential and Membrane Permeability

is the sum of the membrane potential and the electrode potential, the membrane potential was determined by subtracting the electrode potential, $-(RT/F)\ln(a^{\text{I}}/a^{\text{II}})$ from the potential difference. Here, a^{I} and a^{II} are the activities of chloride ion[5] in solutions I and II, respectively.

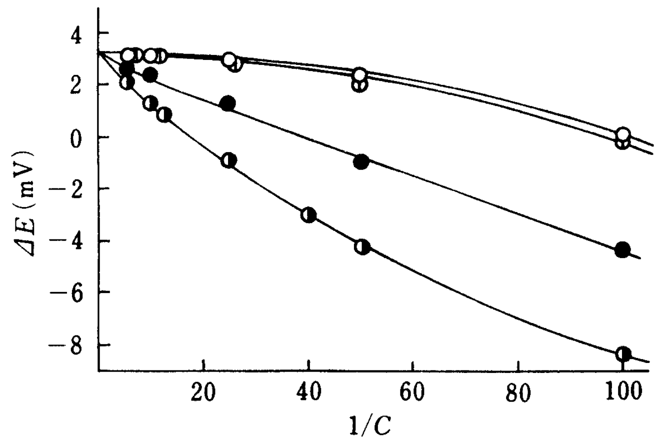

Fig. 2. Plots of Membrane Potential against $1/C$ when $r=2$ at 34°C

W-membrane (○), A-membrane (⦶), M-membrane (●), D-membrane (◑).

The membrane potentials ΔE of water-treated membrane (W-membrane), medium-colored membrane (M-membrane), deep-colored membrane (D-membrane), and auxilliary agent-treated membrane (A-membrane), as explained in "Experimental," were measured in various concentrations of sodium chloride. From these experimental data, the transport number of chloride ion, t_-^*, in the membrane was first determined by plotting (as shown in Fig. 2) the resulting potential ΔE against the reciprocal of the concentration $1/C$. The transport number of chloride ion, t_-^*, in the membrane phase was estimated as 0.586 irrespective of the kind of membrane, when calculated from the limiting potential obtained when $1/C$ approaches 0 according to the eq. (4). As this value is similar to the transport number of chloride ion in water, 0.59, it is considered that the ratio of the mobility of anion to that of cation was hardly affected in any of the membranes. By using the transport number of chloride ion, 0.59, thus obtained, theoretical curves can be drawn for various θ^* values from -1×10^{-3} to -10×10^{-3} mol/l, as shown in Fig. 3, together with the experimental values for W-membrane. The θ^* value which best fits the experimental data for W-membrane, was $\theta^*=-3.5\times10^{-3}$ mol/l. The values of θ^* for other membranes were determined in the same manner and the theoretical curves for these values of θ^* are compared with the experimental values in Fig. 4. The agreement is good except in the region of very low electrolyte concentration. The results thus obtained are given in Table I.

Fig. 5 shows the reduced membrane permeability coefficients, Pr, determined for NaCl and for W-membrane in comparison with the theoretical curves calculated according to eq. (5)

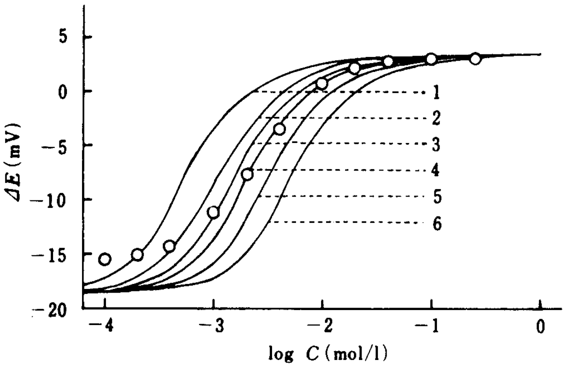

Fig. 3. Theoretical Curves of W-membrane Potentials of NaCl Solution for Various Values of θ^*

1, $\theta^* = -1 \times 10^{-3}$; 2, $\theta^* = -2 \times 10^{-3}$; 3, $\theta^* = -3 \times 10^{-3}$; 4, $\theta^* = -4 \times 10^{-3}$; 5, $\theta^* = -6 \times 10^{-3}$; 6, $\theta^* = -10 \times 10^{-3}$. Experimental values are also plotted. In this case θ^* is equal to -3.5×10^{-3}.

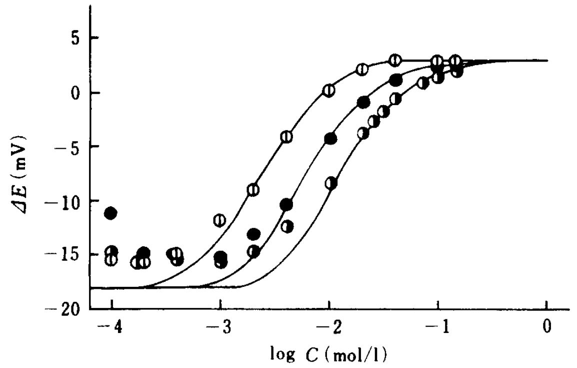

Fig. 4. Plots of Membrane Potentials against log C when $r = 2$ at 34°C

A-membrane (⦶), M-membrane (●), D-membrane (◑).

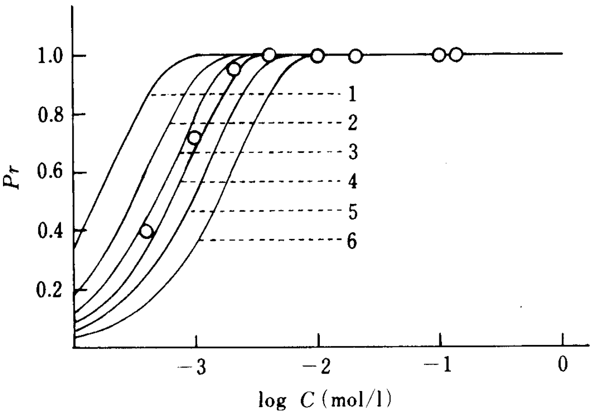

Fig. 5. Theoretical Curves of W-membrane of ReducedMembrane Permeability Coefficients of NaCl Solution for Various Values of θ^*

1, $\theta^* = -1 \times 10^{-3}$; 2, $\theta^* = -2 \times 10^{-3}$; 3, $\theta^* = -3 \times 10^{-3}$; 4, $\theta^* = -4 \times 10^{-3}$; 5, $\theta^* = -6 \times 10^{-3}$; 6, $\theta^* = -10 \times 10^{-3}$. Experimental values are also plotted. Membrane charge density. θ^* that gives the best fit is -3.5×01^{-3}.

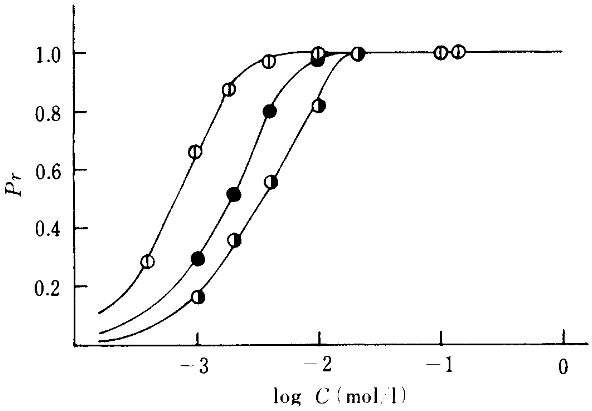

Fig. 6. Plots of Reduced Membrane Permeability Coefficient against log C when $r = 2$ at 34°C

A-membrane (⦶), M-membrane (●), D-membrane (◑).

with various values of θ^* from -1×10^{-3} to -10×10^{-3} mol/l. From the fitting of the experimental data to the theoretical curves, the value of $\theta^* = -3.5 \times 10^{-3}$ mol/l was obtained in this case. The θ^* values for other membranes were determined in the same manner.

The theoretical curves were drawn using these values of θ^* and are compared with the expertimental values in Fig. 6. The results obtained are also given in Table I. The values of θ^* for the four kinds of membranes obtained from the membrane potential agree well with those ob-

TABLE I. Various Measurement Values (θ^*, P_∞, Amount of dye) of the Four Membranes

Membrane	Amount of dye (mol/cm^3)×10^4	θ^*×10^3(mol/l) (from membrane potential)	θ^*×10^3(mol/l) (from membrane permeability)	P_∞×10^6 (cm^2/s)	P_∞/D_0
W-membrane		− 3.5	− 3.5	0.84	0.044
A-membrane		− 4.1	− 4.1	0.87	0.046
M-membrane	0.157	−12	−12	0.83	0.044
D-membrane	0.338	−24	−23	0.86	0.046

tained from the reduced permeability coefficient. The θ^* value of W-membrane is similar to that of A-membrane and the negative charge density increases with increase in the amount of Congo Red dye bound to the membrane (*i.e.*, with deeper color). When the negative change density θ^* of the membrane was plotted against the amount of Congo Red (mol/cm^3) adsorbed on the membrance per unit volume of membrane, a linear relationship was obtained as shown in Fig. 7.

It is concluded, therefore, that the Congo Red adsorbed to the membrane dissociates a sodium ion into the aqueous solution, leaving the residual dye anion in the membrane so that the negative charge density increases with increase in the amount of Congo Red in the membrane.

The membrane charge per unit volume, Q, given in eq. (9), is considered to increase with increase in the amount of dye. Also, as the charge density, θ^*, is a linear function of the amount of dye, it is assumed that the porosity of the membrane is essentially unaffected by the dye.

P_∞ is the membrane permeability coefficient at a sufficiently high concentration; P_∞/D_0, where D_0 is the diffusion constant of sodium chloride in aqueous solution ($D_0=1.89\times10^{-5}$ (cm^2/s)] can therefore be calculated, and the results are listed in Table I. P_∞/D_0, called the apparent membrane constant, is proportional to the degree of porosity of the membrane. The values of the degree of porosity were almost constant irrespective of the amount of Congo Red adsorbed on the membrane. Further, values of porosity of the membrane, which were measured by a liquid substitution method, were approximately constant as shown in Table II. That the degree of porosity of the membrane is constant corresponds well to the fact that the porosity of the membrane is constant.

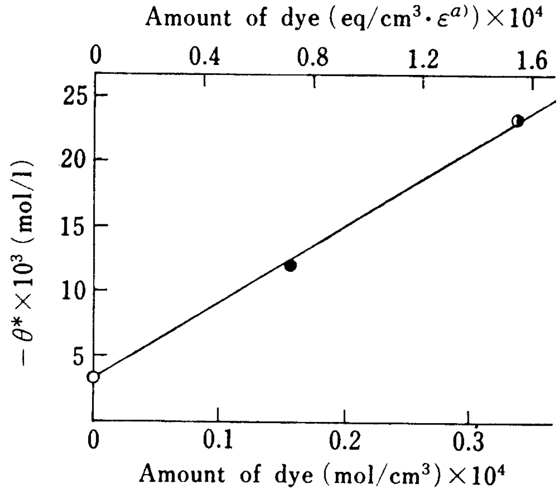

Fig. 7. Plots of Membrane Charge Density against Amount of Dye

W-membrane (○), M-membrane (●), D-membrane (◑).
a) Porosity of membrane.

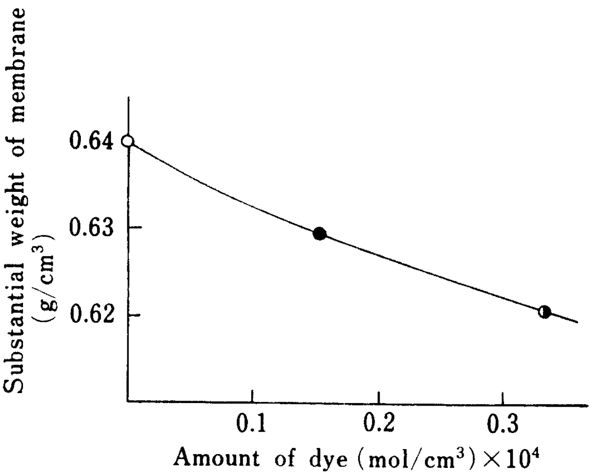

Fig. 8. Relation between Substantial Weight of Membrane and Amount of Dye

W-membrane (○), M-membrane (●), D-membrane (◑).
Substantial weight of membrane is the combined weight of cellulose and bound water.

TABLE II. Values of Porosity of the Four Membranes

Membrane	Volume of membrane (cm^3)	Volume of vacant space of membrane (cm^3)	Porosity of membrane
W-membrane	0.4484	0.1936	0.432
A-membrane	0.5240	0.2290	0.437
M-membrane	0.5245	0.2293	0.437
D-membrane	0.4839	0.2133	0.441

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Part of the water present in natural polymer gel is called bound water, since it is considered to be unable to move freely owing to hydrogen bonding with residual polar groups of the polymer,[6] while the other water is considered to show the same properties as ordinary water, and is thus called free water. Therefore, the cellulose membrane is considered to contain both bound water and free water and the solute is considered to diffuse through the free water.

The weight of membrane, W_m, for the W-membrane and A-membrane is given by eq. (10).

$$W_m = W_c + W_f + W_b \tag{10}$$

Here, W_c, W_f, and W_b represent the weights of cellulose, free water, and bound water, respectively. The weight of membrane, W_m, for the M-membrane and D-membrane is given by eq. (11).

$$W_m = W_c + W_f + W_b + W_d \tag{11}$$

where W_d is the weight of dye. The weight in eq. (10) and (11) represents the weight per unit volume of membrane. From the measurements of porosity (Table II), the substantial weight of membrane ($W_c + W_b$) was estimated and plotted against the amount of dye (Fig. 8). The substantial weights of M-membrane and D-membrane decreased with increase of the amount of dye attached to the membrane, in comparison with those of W-membrane and A-membrane. Taking into consideration that the porosities of the four membranes are approximately constant, these results suggest that the bound water is replaced by dye molecules.

In Fig. 7, the charge densities of the membranes θ^* are plotted against the amount equivalent of Congo Red per unit volume of vacant space estimated from eq. (9). The slope of this straight line, corresponding to the degree of dissociation of Congo Red, is calculated to be about 12.6%. It is considered that Congo Red dissociates almost completely in aqueous solution, but when adsorbed on the membrane, it exhibits the same properties as a polymer electrolyte and sodium ion is incorporated into the membrane, and the degree of dissociation of Congo Red decreases substantially.[7]

Experimental

Materials——Four kinds of membranes were used. Visking cellulose tubing was immersed in boiling water for 12 h and washed well with water; the resulting membrane is referred to as the water-treated membrane (W-membrane). The W-membrane was dyed by heating it at 95—100°C for 0.5 h in a solution containing 2% Congo Red, 1.5% $Na_2CO_3 \cdot 10\ H_2O$ and 15% $Na_2SO_4 \cdot 10\ H_2O$ with respect to the membrane, and at a ratio of membrane to water of 1 : 50; the resulting membrane is referred to as medium-colored membrane (M-membrane). The W-membrane dyed with 5% Congo Red. 2.0% $Na_2CO_3 \cdot 10\ H_2O$, and 30% $Na_2SO_4 \cdot 10\ H_2O$ for 1 h, other conditions being the same as in the case of M-membrane, is referred to as deep-colored membrane (D-membrane). The W-membrane treated under the same conditions as in the case of the deep-colored membrane without addition of the dye is referred to as the auxiliary agent-treated membrane (A-membrane). The thickness of the membrane was measured with a dial thickness gauge with an accuracy of ±0.001 mm. NaCl used was obtained by drying NaCl of reagent grade at 150°C for 34 h. Congo Red, reagent grade, was used without further purification. Water that had been deionized and doubly distilled was used throughout this experiment.

Measurement of the Membrane Potential——The Ag–AgCl electrode[8] used was prepared by winding a platinum wire 5 cm long in a spiral,plating the resulting spiral wire with silver in a solution of $AgK(CN)_2$ (1 g/100 ml) for 6 h, washing the resulting product sufficiently with distilled water, and electrolyzing it further at a current density of 1 mA/cm^2 in 0.1 N HCl for 0.5 h to convert part of the Ag into AgCl. The electrometer used was a TR-8651 electrometer manufactured by Takeda Riken Co., Ltd.

Measurement of the Membrane Permeability Coefficient——Changes with time in the conductivity of the solutions in the two chambers of the cell divided by a membrane were measured and the changes in the concentration of the solutions were measured using a calibration curve that had previously been obtained; thus, the membrane permeability coefficient P was determined according to eq. (6) since the flux J of the solute across the membrane was determined. Conductivity was measured with a universal bridge, model 4225A, manufactured by Yokogawa-Hewlett-Packard Co., Ltd. All the experiments were conducted at 34°C.

Measurement of the Amount of Dye adsorbed on the Membrane——The concentration of dye in the dye bath was determined colorimetrically from a calibration curve that had previously been obtained; the amount of dye adsorbed in the membrane was determined from the difference between the initial and final concentrations of the dye in the solution. The colorimetry was carried out with a Shimadzu UV 200 spectrometer at a wavelength of 497 nm.

Measurement of the Porosity——The membrane, which had been dried in a constant-temperature drying apparatus at 105°C to constant weight, was soaked in water. After the water on the surface of the membrane had been sufficiently wiped off, the increase in weight of the membrane was measured and the total vacant volume was determined by dividing the weight increase by the density of water, based on the assumption that all the weight increase is ascribable to water entering the pores of the membrane.

References and Notes

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