특별강연 II

용질배제 곡선에 의한 한외여과 막의 세공특성 예측

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Prediction of Intrinsic Pore Properties of Ultrafiltration Membrane by Solute Rejection Curves

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1. Introduction

The characterization of pore properties (mean pore size and pore size distribution) of the active layer in a UF membrane is important not only in order to obtain information about the factors affecting pore formation during membrane manufacturing but also to understand deeply the mechanism of solute and solvent transport through pores. Many methods of characterizing quantitatively the pore properties of UF membranes have been suggested in the literature: solvent and gas flow measurement, bubble point determination, electron microscopy, gas adsorption/desorption measurement, rejection measurement *etc.* But most of these methods involve time-consuming procedures and involve some wellknown problems and uncertainties.

Because of its simplicity, the rejection measurement is being used widely as a method to characterize UF membrane. In this method, the pore properties are described by a molecular weight cut-off and/or a solute rejection curve. Michaels reported that the solute rejection curve - the variation of solute rejection with Einstein-Stokes radius of the permeating solutes - yielded straight line on log normal probability paper and the pore properties were defined by two characteristic parameters: the mean value(mean molecular size) and the standard deviation. The limitations of the rejection measurement method are that the rejections vary with the operating conditions, which may cause the concentration polarization, and that the mean value does not define exactly the mean pore size of the UF membrane.

In this report, develop a method exactly describing the pore properties(mean pore size and pore size distribution) of UF membrane from the rejection curves by correcting the steric and hydrodynamic hindrance effect of pores on molecules. Furthermore, the effects of operating conditions(pressure, feed concentration and recirculation velocity) on the pore properties are examined and are eliminated by extrapolating to the "zero" operating conditions for obtaining the apparent intrinsic pore properties which are insensitive to the operating conditions.

2. Theoretical

For an UF membrane having a uniform pore diameter D_p, Zeman and Wales expressed the solute rejection in terms of ($\lambda = D_s/D_p$, solute to pore diameter ratio) accounting the steric and hydrodynamic hindrance effect of the pore on molecules whose diameters approach to pore diameter:

$$R_t = 1 - \{1 - [\lambda(\lambda - 2)]^2\} \exp(-0.7146\lambda^2) \tag{1}$$

If solute rejection correlates with solute diameter by the log normal probability function, this relationship is expressed as:

$$R_t = \text{erf}(y) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{y} e^{-u^2/2} du \tag{2}$$

where

$$y = \frac{\ln D_s - \ln \bar{D}_s}{\theta} = \frac{\ln D_s - \mu}{\theta} \tag{3}$$

and $\bar{D}_s$, μ are the mean solute diameter and the mean at R_t = 0.5 respectively, and θ is the standard deviation about μ. μ and θ are expressed as:

$$\mu = \ln D_s = (\ln D_s)_{Rt=0.5} \tag{4}$$

$$\theta = \frac{(\ln D_s)_{Rt=0.841} - (\ln D_s)_{Rt=0.159}}{2} \tag{5}$$

To describing more exactly the pore properties of UF membrane, we determine the mean pore diameter $\bar{D}_p$ from Eqs.(1) and (4) by correcting the steric and hydrodynamic hindrance effect of pore on molecules. In Eq.(1), assuming that the pore diameter representing 50% rejection is the mean pore diameter $\bar{D}_p$ of UF membrane, we obtain the value of the $\bar{D}_s$ to $\bar{D}_p$ ratio. This value is 0.416 at R_t = 0.5. From Eq.(4), hence, the mean pore diameter D_p is expressed as:

$$\bar{D}_p = \frac{1}{0.416}\exp(\mu) \tag{6}$$

From $\bar{D}_p$ and θ, the pore size distribution of UF membrane is expressed as the following probability density function.

$$\frac{dF(D_p)}{dD_p} = \frac{1}{D_p\theta\sqrt{2\pi}}\exp\left[-\frac{(\ln D_p - \ln \bar{D}_p)^2}{2\theta^2}\right] \tag{7}$$

3. Experimental

The UF membrane used was a polysulfone flat type, SEPA-PS-O (molecular weight cut-off = 3,000) supplied by Osmonics, Ltd., USA. Three polyethylene glycols(PEG, Union Carbide Co., USA) and four dextrans(Fluka AG., Switzerland) were used as test solutes. The characteristic properties of seven solutes are shown in Table 1. The UF cell was a thin channel type with a height of 0.34 cm, and had an effective membrane area of 32.67 cm^2 (length 14.85 cm x width 2.2 cm). Inlet and outlet region of the UF cell were designed to minimized the flow effects at membrane surface. The experimental conditions are listed in Table 2.

Table 1. Characteristic properties of PEG and dextran solutes (at 35°C)

Solutes	M_w	M_n^*	$[\eta]^* \times 10^3$ [kg/m^3]	D_s [Å]
PEG 1,500	1,780	1,330	7.66	25.86
PEG 4,000	4,010	3,400	12.25	39.64
PEG 6,000	7,000	6,280	17.39	53.64
Dextran 20T	17,500	15,520	12.94	65.98
Dextran 40T	40,000	35,860	19.56	99.75
Dextran 70T	70,000	51,630	25.88	131.95
Dextran 110T	110,000	73,350	32.44	165.41

Table 2. Experimental conditions in ultrafiltration of PEG and dextran solutions

Pressure [10^5 Pa]	0.49, 0.98, 1.47, 1.96, 2.94, 3.92
Feed concentration [kg/m^3]	3.53, 6.57, 10.35, 13.56
Recirculation velocity [m/s]	0.2, 0.3, 0.4, 0.5, 0.6
Temperature [°C]	35±0.2

4. Results and Discussion

The variation of the true rejection with solute diameter (solute rejection curve) on log normal probability paper are represented in Fig. 1. All solute rejection curves on log normal probability paper yield straight lines. In Fig. 1, the slope of straight lines is decreases and the intercept is increases with increasing pressure and feed concentration, but the slope and intercept do not vary with recirculation velocity.

For each pressure and feed concentration, the values of μ, θ and $\bar{D}p$ are listed in Table 3. Table 3 predict that the pore property parameters are varied with change of pressure and feed concentration. Thus obtaining the apparent intrinsic pore properties of SEPA-PS-0 membrane which are insensitive to operating conditions, the pore property parameters are extrapolated to zero-pressure and zero-feed concentration state. This values are also listed in Table 3. The pore diameter distribution curve of SEPA-PS-0 membrane obtained using these parameters at free pressure and free feed concentration state is represented in Fig. 2. This distribution curve can be considered as a representation of the apparent intrinsic pore diameter distribution of SEPA-PS-0 membrane. The mean pore diameter of SEPA-PS-0 membrane is about 60 Å and the pore diameter distribution range from 30 Å to 103 Å in 99% confidence level.

MW.

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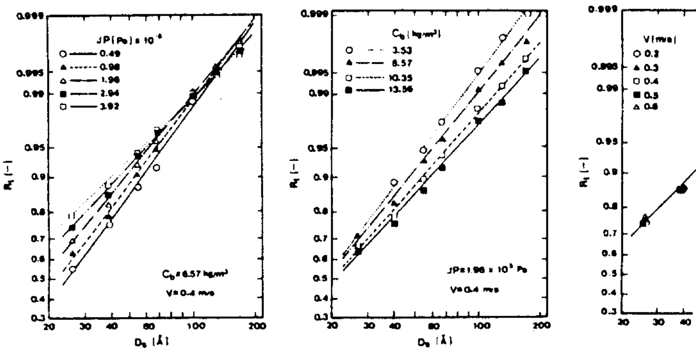

Fig. 1. Solute rejection curves on log normal probability graph

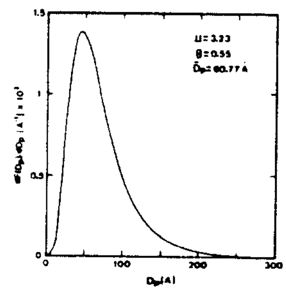

Fig. 2. Pore size distribution of SEPA-PS-0 membrane

Table 3. Pore property parameters for SEPA-PS-0 membrane at different pressures and feed concentrations

C_b [kg/m³]	Parameters	ΔP[Pa] × 10^{-5}						
		Free pressure state	0.49	0.98	1.47	1.96	2.94	3.92
Free concentration state	μ	3.23	3.11	3.04	2.91	2.89	2.62	2.42
	θ	0.55	0.56	0.60	0.60	0.61	0.63	0.70
	$\bar{D}_p$	60.77	53.90	50.25	44.13	43.25	33.02	27.03
	r	—	—	—	—	—	—	—
3.53	μ	3.32	3.22	3.10	2.99	2.93	2.68	2.47
	θ	0.56	0.58	0.61	0.63	0.65	0.68	0.76
	$\bar{D}_p$	66.49	60.16	53.36	47.80	45.02	35.06	28.42
	r	—	0.992	0.996	0.999	0.999	0.993	0.992
6.57	μ	3.36	3.25	3.16	3.01	2.95	2.71	2.51
	θ	0.56	0.60	0.66	0.70	0.73	0.83	0.92
	$\bar{D}_p$	69.21	62.00	56.66	48.77	45.93	36.13	29.58
	r	—	0.998	0.998	0.998	0.998	0.998	0.997
10.35	μ	3.45	3.38	3.21	3.07	2.98	2.78	2.54
	θ	0.57	0.63	0.68	0.74	0.78	0.89	1.01
	$\bar{D}_p$	75.72	70.60	59.57	51.78	47.33	38.75	30.48
	r	—	0.998	0.998	0.996	0.997	0.996	0.991
13.56	μ	3.54	3.47	3.28	3.16	3.04	2.82	2.61
	θ	0.58	0.64	0.69	0.75	0.81	0.93	1.05
	$\bar{D}_p$	82.85	77.25	63.88	56.66	50.25	40.33	32.69
	r	—	0.997	0.997	0.997	0.995	0.995	0.995