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Posttreatment Effects on Pore Size Distribution of Loeb-Sourirajan-Type Modified Cellulose Acetate Ultrathin Membranes

HARUHIKO OHYA, HOZUMI KONUMA,* and YOICHI NEGISHI,
Department of Chemical Engineering, Yokohama National University, Yokohama, Japan

Synopsis

The nitrogen gas adsorption isotherms at −195°C on modified cellulose acetate ultrathin membranes were measured, and the surface area of the pores was determined by the method employed by Cranston and Inkley. A relationship between reverse osmosis characteristics and the mean pore radius was correlated, and it was observed that any method (such as longer evaporation period, heat treatment, or reduction of swelling agent) reducing the mean pore radius to below 20–22 Å improves membrane characteristics of reverse osmosis separation significantly.

INTRODUCTION

The porous structure of Loeb-Sourirajan-type cellulose acetate membranes was examined by electron microscopy by Riley et al.[1,2] They confirmed that the membrane consists of a dense, thin surface layer on the film side exposed to air during casting, with a highly porous substructure underneath the surface layer. This dense, thin surface layer plays a significant role in reverse osmosis separation.

There have been many discussions on the structure of the surface layer. Riley et al.[1,2] reported that it was devoid of structural characteristics, showed no evidence of pores greater than 100 Å, and has a thickness of about 0.25 μm. Several workers[1,2,3] reported on its thickness: Schultz and Asunmaa[4] reported that there were pores of average radius 23 Å between cellulose acetate crystallites of size 188 Å.

Several attempts have been made to obtain an ultrathin membrane consisting of only a dense, thin cellulose acetate membrane. For example, Riley et al.[5] prepared ultrathin membranes using the Carnell-Cassidy technique,[6,7] which consists essentially of slowly withdrawing a clean glass plate from a dilute solution of a polymer in a suitable solvent. Their membrane was devoid of porous structure, and an effort was made to obtain as thin a membrane as possible to increase water flux.

Ohya et al.[8] showed that there are no pores in the ultrathin membrane cast

* Present address: Central Research Laboratory, Ebara Mfg. Co., LTD., Fujisawa City, Kanagawa, Japan.

TABLE I
Composition, Physical Properties, Pore Volume, Surface Area, and Reverse Osmosis Characteristics of Membranes[a]

Batch no.	Ratio of cellulose acetate to 10% $Mg(ClO_4)_2$ aqueous soln.	Weight fraction of cellulose acetate	Viscosity cp	Density, g/cm³	Superficial surface area of membrane, m²/g	Estimated membrane thickness, μm	Surface area of pores, m²/g	Mean pore radius based on cross-sectional area, Å
K-1	5:0.0	0.04843	4.10	0.8013	1.885	0.408	0.0	0.0
K-2	5:0.1	0.0482	10.61	0.8290	1.360	0.539	13.9	19.8
K-3	5:1	0.0482	16.65	0.8359	0.9385	0.941	16.4	20.4
K-4	5:5	0.0482	19.28	0.846	0.8738	1.096	19.3	21.2
K-5	5:18	0.0482	41.34	0.8988	0.5645	1.754	58.8	21.8

	Percent cross-sectional area of pore open on membrane, %	Flux, g/cm²·hr		Salt separation, %	
		Air side in contact with salt solution	Glass side in contact with salt solution	Air side in contact with salt solution	Glass side in contact with salt solution
K-1	0.0	0.067	0.060	95.5	87.5
K-2	4.68	0.62	0.37	79.5	74.4
K-3	2.88	4.22	4.31	44.4	19.4
K-4	6.72	3.85	5.53	18.4	18.4
K-5	8.68	—	—	—	—

[a] Evaporation period 4.5 min, without heat treatment.

from a solution of cellulose acetate in acetone, but that there do exist pores in the modified ultrathin membrane from a solution of cellulose acetate in acetone and a swelling agent, formamide. This modified ultrathin membrane about 1 μm thick, shows symmetric characteristics of good separation and higher permeability than the ultrathin membrane 600 Å thick by Merten et al.[5]

It is the purpose of this paper to obtain a relationship between pore size distribution and the reverse osmosis characteristics of the modified ultrathin membranes.

EXPERIMENTAL

The Modified Ultrathin Membrane

A number of the modified Loeb-Sourirajan-type ultrathin membranes were prepared, using almost the same method reported earlier,[8] from casting solutions whose compositions are shown in Table I. The temperature of the casting solution was kept at 1–2°C, the ambient temperature at 20°C, and the ambient humidity at 50%. Membrane thickness was estimated by the following equation[8] using withdrawal rate, measured physical properties of the casting solutions, and the density of the porous ultrathin membranes:

$$\bar{\delta} = 0.4 \frac{\rho_L}{\rho_S} W_S \sqrt{\frac{\mu u_0}{\rho g}} \tag{1}$$

The evaporation period was 2 to 12 min. Even a 2-min period gave a symmetric, modified, ultrathin membrane as shown in Table II. The membranes, having a 37-cm^2 area, were floated off each surface of the glass plate onto the surface of the water and stored wet. After more than 30 leaves of membranes were collected, thermal treatment was used at a designated temperature in a water bath for 20 min. After the thermal treatment, the membranes were freeze dried as reported earlier.[8]

Adsorption Isotherms

The adsorption isotherms of the freeze-dried membrane at −195°C were determined on a standard Emmett and Brunauer apparatus. The gas used was

TABLE II
Effects of Evaporation Period on Reverse Osmosis Characteristics[a]

Evaporation period, min	PWP, g/hr		Salt separation, %	
	Air side in contact with pure water	Glass side in contact with pure water	Air side in contact with salt solution	Glass side in contact with salt solution
1.0	32.97	34.41	22.2	51.4
2.0	37.65	37.71	42.9	40.0
3.0	43.95	46.43	44.8	44.8
4.5	41.78	46.12	44.4	19.4
6.0	37.59	48.52	41.7	30.6
8.0	54.4	45.38	31.6	26.3
10.0	42.61	42.06	40.5	32.4
15.0	11.30	11.35	75.68	75.68

[a] Casting solution Batch K-3, without heat treatment.

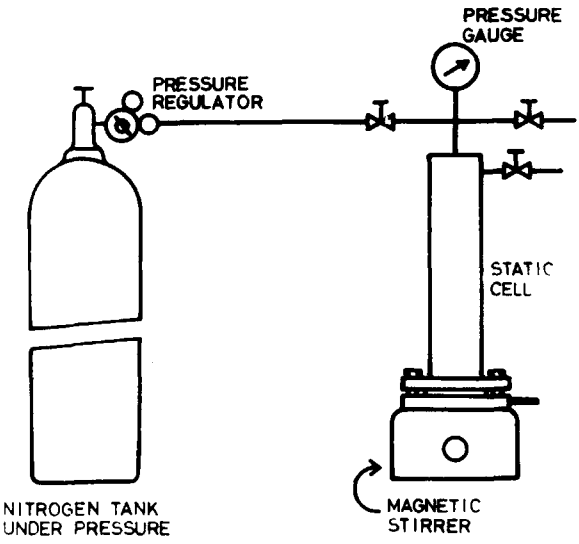


Fig. 1. Reverse osmosis cell assembly.

prepurified nitrogen dried through a cold trap and cooled to liquid nitrogen temperature.

Reverse Osmosis

The reverse osmosis experiments with the modified ultrathin membranes were carried out at laboratory temperature at a pressure of 20 kg/cm^2 g, using the reverse osmosis cell shown in Figure 1.

Other experimental procedures were conducted in the manner previously reported.[8]

RESULTS

Isotherms of Freeze-Dried Membranes

Figure 2 gives the experimental isotherms of five different kinds of freeze-dried Loeb-Sourirajan-type modified ultrathin membranes without thermal treatment at −195°C. Figure 3 gives the experimental isotherms of five kinds of freeze-dried modified ultrathin membranes with varying evaporation periods and thermal treatment temperatures. The data of batch K-2 in Figure 2, expressed as a B.E.T. plot in Figure 4, yields a pore surface of 10.2 m^2/m^2 of membrane area. The latter was estimated from the B.E.T. equation from the nitrogen isotherm, using 16.2 Å^2 as the area occupied by each adsorbed nitrogen molecule. Similar calculations were done for batch K-3 to K-5, and some of the results are shown in Table I.

The ultrathin membrane batch K-1, obtained from the cellulose acetate–acetone solution, was the only one that did not adsorb nitrogen at all.[8]

Reverse Osmosis

Results obtained in batches K-1 to K-4 of the ultrathin membranes which were used without thermal treatment are also presented in Table I. Membranes of

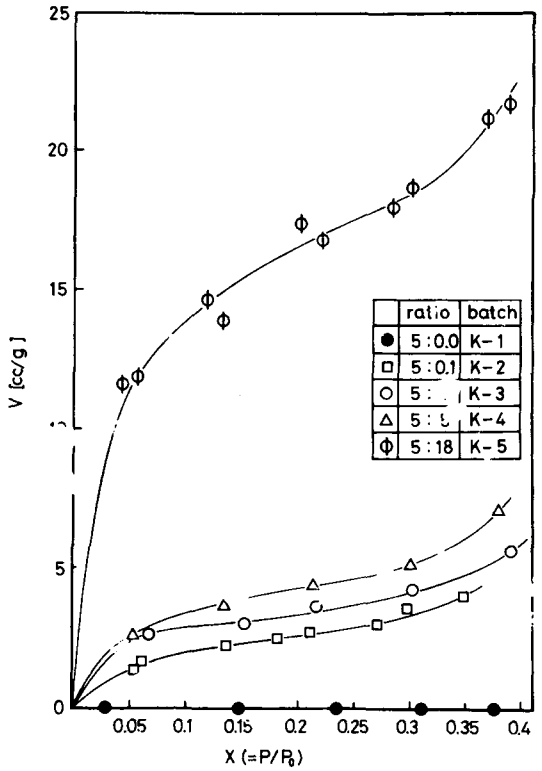


Fig. 2. Nitrogen gas adsorption isotherms for one ultrathin and four modified ultrathin membranes at −195°C. Withdrawal rate u_0 = 0.224 cm/sec, no heat treatment, evaporation period 4.5 min; the ratio in figure is that of cellulose acetate to 10% aqueous magnesium perchlorate.

composition K-5 were too fragile to be handled; therefore, reverse osmosis experiments were not carried out with these membranes. Reverse osmosis tests were carried out to verify the symmetry of the ultrathin membrane as follows: Two membranes were chosen at random from about 50 samples composed on both sides of the glass plate which was withdrawn from the casting solution. One membrane, facing air, was set in a reverse osmosis test cell in the high-pressure salt solution at 20 kg/cm^2 g, while the other facing the glass side, was set. If the membranes were asymmetric, we could not obtain the same pure-water flux rate and salt rejection.

But as shown in Tables I and II, the pure-water flux rate and the salt rejection are almost the same for the data obtained on both sides. Hence, we might say that the ultrathin membranes obtained by this procedure are symmetric membranes.

DISCUSSION

Pore Size Distribution

The pore size distribution of the freeze-dried membranes was determined by the method of Cranston and Inkley[9] using low-temperature adsorption isotherms. The volume of the pores for each pore size range was calculated. The cross-

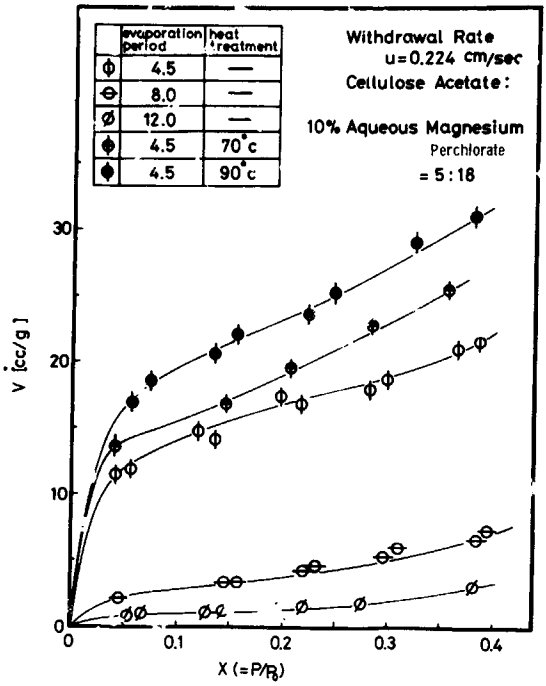


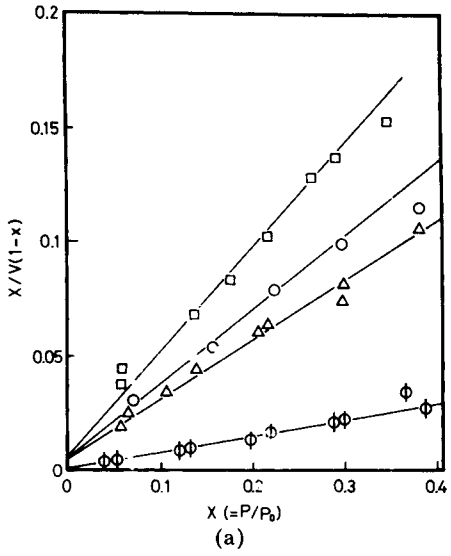
Fig. 3. Nitrogen gas adsorption isotherms for five modified ultrathin membranes at −195°C, varying three evaporation periods and heat treatment temperatures.

sectional area assigned to the pores of each radius was calculated assuming that all pores were straight cylindrical, perpendicular to the membrane surface, and that the length of each pore was the same as the thickness of the membrane calculated by eq. (1).

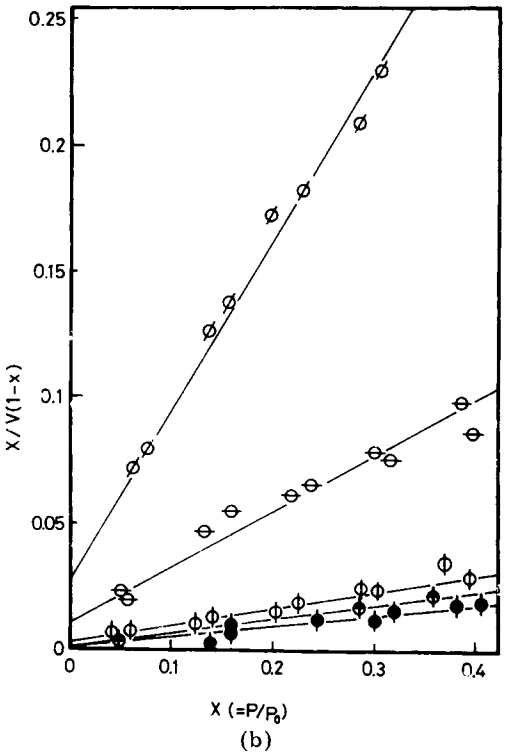
For batch K-2 (cellulose acetate: 10% aqueous magnesium perchlorate = 5:0.1), with evaporation period 4.5 min and no thermal treatment, the total cross-sectional area of the pores was 468 cm^2 per m^2 of membrane surface, which corresponds to 4.68% of membrane surface. For batch K-1 (cellulose acetate:10% aqueous magnesium perchlorate = 5:0), there were no pores.[8]

Effects of Composition

The increase in the amount of 10% aqueous magnesium perchlorate in the casting solution corresponds to an increase in water flux through the membrane from 0.06 g/cm^2·hr to 4–5 g/cm^2·hr up to a ratio of 5:1, but to a steady decrease in salt rejection from 95 to 18%. From the adsorption isotherm shown in Figure 2, there are no pores at all on the ultrathin membrane cast from the solution composed of cellulose acetate and acetone containing no aqueous magnesium perchlorate. Its structure is dense and might be assumed to be homogeneous judging from the identical results obtained on the reverse osmosis tests for both sides of the membrane. Batch K-2 to K-4 were obtained with the addition of 10% aqueous magnesium perchlorate to the above solution. The 10% aqueous magnesium perchlorate content of the latter solution was increased from zero



(a)



(b)

Fig. 4. (a) B.E.T. plots for the adsorption of nitrogen gas on modified ultrathin membranes shown in Fig. 2. (b) B.E.T. plots for the adsorption of nitrogen gas on modified ultrathin membranes shown in Fig. 3.

to 5 parts per part of cellulose acetate; this modification of the ultrathin membranes increased the porous structure of the membranes.

The water flux and salt separation at a pressure of 20 kg/cm^2 g were essentially identical with the air side and the glass side of the membrane facing the high-

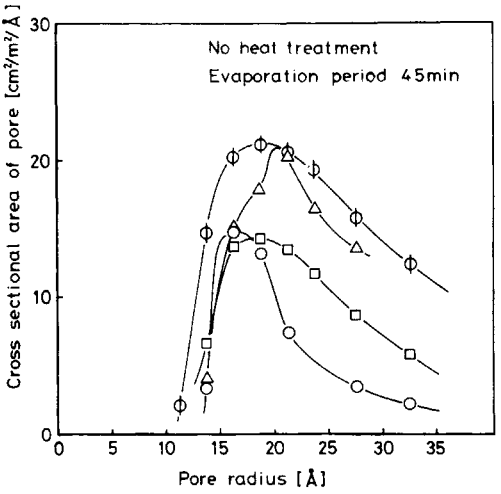


Fig. 5. Distributions of cross-sectional area of pores in ultrathin membranes. Symbols same as in Fig. 2.

pressure solution in all cases. These results show that porous structure of the membrane used was not asymmetric.

When the 10% aqueous magnesium perchlorate content of the casting solution increased from 0.1 to 5 parts per part of cellulose acetate, the salt separation decreased greatly from 80 to 18%, with a slight increase in the mean pore radii from 19.8 to 21.2 Å, and with an increase in the percent cross-sectional area of

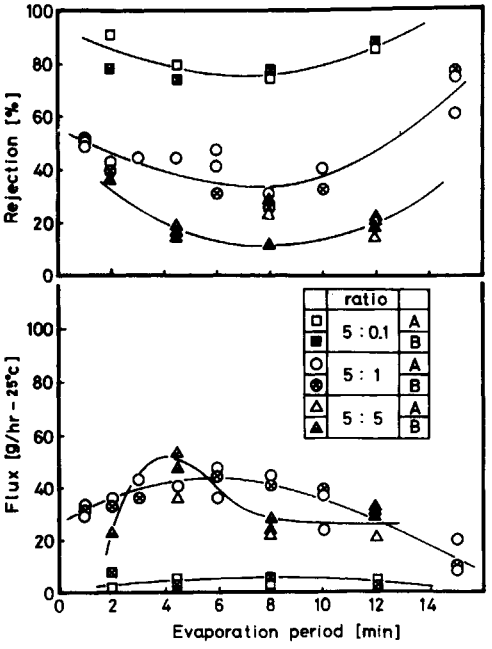


Fig. 6. Relationship between reverse osmosis characteristics and evaporation periods for batches K-2, K-3, and K-4: (a) air side in contact with salt solution; (b) glass side in contact with salt solution; symbols same as in Fig. 2.

TABLE III
Effects of Evaporation Period and Composition of Casting Solution on Surface Area of Pores and Average Diameter[a]

Batch no.	Evaporation period, min	Surface area of pores based on B.E.T. equation, m^2/g	Average pore diameter, Å	Percent pore cross-sectional area, %
K-2	4.5	13.9	41.51	4.68
K-3	2.0	10.9	36.67	2.43
	4.5	16.4	43.05	2.88
	8.0	6.9	50.59	3.30
K-4	4.5	19.3	48.38	6.72
	8.0	8.2	45.65	2.93
K-5	4.5	58.8	48.44	8.68
	8.0	20.7	53.67	4.88
	12.0	7.0	51.47	3.29
	15.0	essentially no nitrogen absorption		

[a] Without heat treatment.

the pores open on the membrane from 4.68 to 6.72%. The water flux through the membrane increased about eightfold from 0.06 to 0.5 $g/cm^2 \cdot hr$ with addition of a small amount of 10% aqueous magnesium perchlorate by 0.1 parts of cellulose acetate and also about eightfold from 0.5 $g/cm^2 \cdot hr$ to 4.3 $g/cm^3 \cdot hr$ by 0.9 parts of cellulose acetate. But further addition of 10% aqueous magnesium perchlorate by 4 parts of cellulose acetate caused a very small increase in water flux. The total cross-sectional area of pores per unit area membrane surface passed through a minimum value of the ratio of 5:1 and then increased as shown in Table I.

The distribution of the cross-sectional area of pores for four different kinds of composition without heat treatment are shown in Figure 5. Comparing the two curves of the pore size distribution for the ratios 5:0.1 and 5:1, it can be seen that the value of the pore radius (or the cross-sectional area of pores on the membrane) at the maximum is higher and its shape narrower for the curve of ratio 5:1 than for the curve of ratio 5:0.1. These two facts indicate that there were a few larger pores, but many more smaller pores, resulting in an average pore size of smaller radius in the modified ultrathin membranes from the 5:0.1 casting solution than from the 5:1 casting solution.

Evaporation Period

Figure 6 shows a relationship between the reverse osmosis characteristics and the evaporation periods for batches K-2, K-3, and K-4. Salt separation curves pass through a minimum around 8 min in the evaporation period for the three batches. Minimum values of salt separation were 75% for batch K-2, 29% for batch K-3, and 12% for batch K-4. On the other hand, the curve of the water flux through the membrane has a maximum. Batch K-2 takes a maximum value of water flux at about 8 min of the evaporation period, batch K-3 at about 6 min, and batch K-4 at approximately 4 min. It might also be derived from Figure 6 that the membranes cast under the conditions investigated in the figure were not asymmetric.

Table III lists the variation of the surface area of the pores based on the B.E.T.

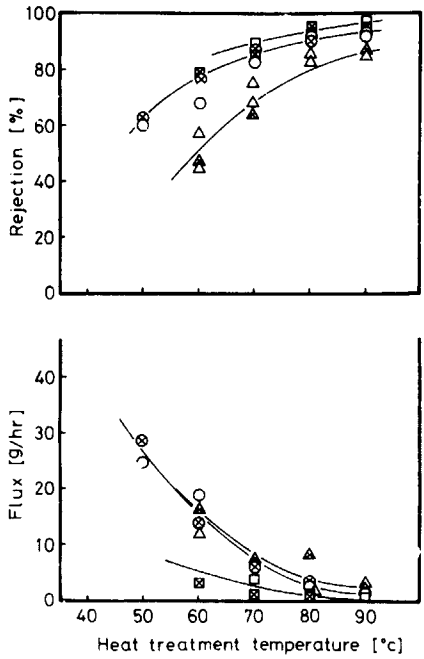


Fig. 7. Relationship between reverse osmosis characteristics and heat treatment temperatures. Symbols same as in Fig. 6.

equation and the mean pore radii against the evaporation period for batches K-2 to K-5. When increasing the evaporation period, the pore surface area showed a tendency to pass through a slight maximum around 4.5 min and then decreased. Especially for the modified ultrathin film cast from the 5:18 ratio casting solution, the pore surface area decreased to almost zero 15 min into the evaporation period.

In an early stage of evaporation, micelles of the swelling agent began to separate from the casting solution. This was caused by condensation of water vapor from the air on the membrane surface because the glass plate had been immersed in the casting solution at 1–2°C. Thus, the micelles might be much smaller and dispersed. Hence, when the mean pore radii are smaller, the micelles might coalesce to become larger, and the number of micelles might be reduced, because of the depletion of evaporated acetone. The mean pore radii then increased until 8 min as shown in Table III. Thereafter, the radii again decreased. This phenomenon of the changes of the mean pore radius explains the existence of a minimum on the curve of the reverse osmosis separation, and a maximum on the water flux in Figure 6.

Heat Treatment Effects

Figure 7 shows the relationship between reverse osmosis characteristics and temperature of thermal treatment for batches K-2, K-3, and K-4. When the temperature of thermal treatment is increased, salt separation is improved and water flux decreases for every batch. This is always observed on a typical asymmetric reverse osmosis membrane of cellulose acetate. The improvement

TABLE IV
Effects of Heat Treatment on Surface Area of Pores and Averaged Pore Diameter[a]

Batch no.	Temperature of heat treatment, °C	Surface area of pores based on B.E.T. equation m^2/g	Averaged pore diameter, Å	Percent cross-sectional area of pores, %
K-2	—	13.9	41.51	4.68
	90	27.3	36.58	5.89
K-3	—	16.4	43.05	2.88
	70	22.7	34.69	2.99
	90	40.3	35.23	4.90
K-4	—	19.3	48.38	6.72
	90	31.0	41.58	5.74
K-5	—	58.8	48.44	8.68
	70	76.3	36.74	9.54
	90	96.7	28.44	10.49

[a] Evaporation period 4.5 min.

is significant in batch K-4, not very significant in batch K-2, and fairly significant in batch K-3.

Heat treatment above 70°C makes the modified ultrathin membranes of batches K-2 to K-5 adsorb more nitrogen or have smaller pores and more pore surface area, as shown in Table IV. This phenomenon may reasonably explain the tendency of reverse osmosis separation and flux shown in Figure 7. As stated by Sarbolonski,[10] cellulose acetate segments seem to move easily above 65°C, and to rearrange their position, resulting in the formation of smaller pores and increasing their numbers due to increasing surface area and decreasing average

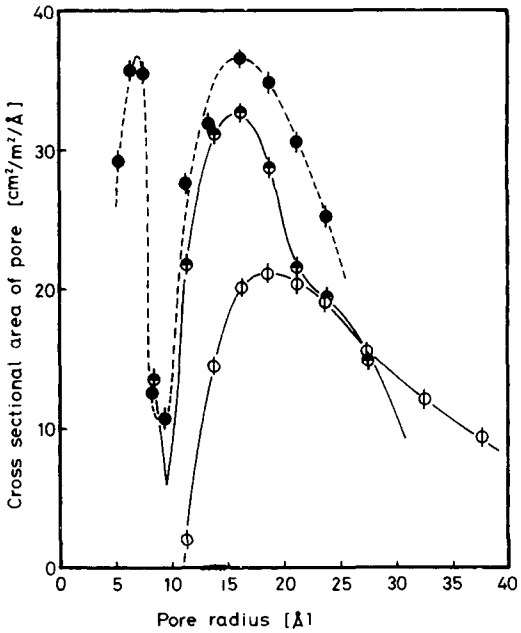


Fig. 8. Effects of heat treatment on pore size distribution for batches K-5. Symbols same as in Fig. 3.

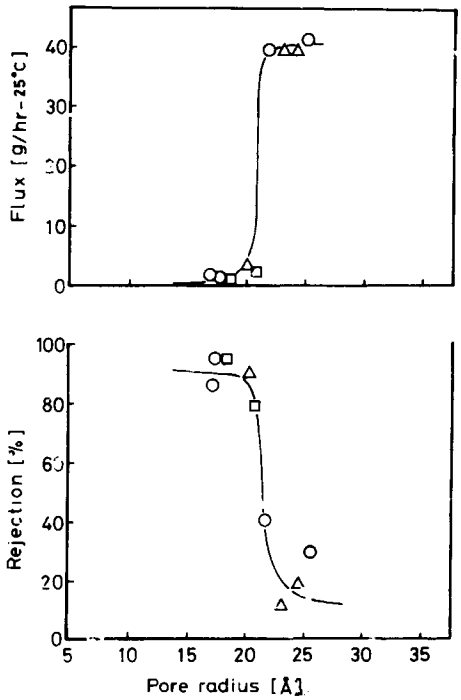


Fig. 9. Effects of pore size on reverse osmosis characteristics of modified ultrathin membranes. Symbols same as in Fig. 2.

pore diameter. Note in particular that the shape of the pore size distribution for the ultrathin membrane cast from the 5:18 casting solution shifts from a single peak in the case of no heat treatment to a twin peak by the heat treatment, as shown in Figure 8. The average pore radii corresponding to the twin peaks are 8 and 15.2 Å at 70°C, and 7 and 15.5 Å at about 90°C. The number of pores assigned to the smaller pore radius is larger at 90°C than at 70°C.

These phenomena might be reasonably explained as follows. The as-cast ultrathin membrane from the 5:18 casting solution has a broader pore size distribution and a larger average pore radius. Application of thermal treatment makes cellulose acetate segments rearrange themselves, but the larger pores might remain because the intersegmental forces are not sufficient. Then, the rather small and medium pores shift to the smaller pores and the larger pores remain unchanged, so smaller pore groups and larger pore groups appear. The pore size distribution has two peaks; and as the temperature increases, the smaller peak becomes smaller and the larger one increases.

Manjikian and Foley[11] observed an increase of iodine absorption by the cellulose acetate butyrate membrane with increasing thermal treatment temperature. They showed that heat treatment resulted in an expansion of membrane pores through shrinkage of surrounding membrane material away from the pore area and that this increase in pore size was reflected in the degree of iodine adsorption.

It may be concluded from the increase in amount of nitrogen adsorption at −195°C and the decrease of the pore size with increasing thermal treatment temperature, as shown in Table IV, that thermal treatment may result in an

increase in the number of small pores through shrinkage of the membrane matrix.

Reverse Osmosis Characteristics and Average Pore Radius

A relationship between reverse osmosis characteristics of a modified ultrathin membrane and its average pore radius is shown in Figure 9. The water flux and the salt separation change abruptly at an average pore radius of 20–22 Å. Any method (longer evaporation period, heat treatment, or reduction of swelling agent) which lets the average pore radius shrink below 20–22 Å improves the reverse osmosis characteristics of the modified ultrathin membrane. This critical pore radius is identical to that reported by Ballow[12] on porous glass reverse osmosis membranes and that by Sourirajan and Agrawal[13] on freeze-dried cellulose acetate membranes.

CONCLUSIONS

The results presented in this paper show that the presence of 10% aqueous magnesium perchlorate in the casting solution leads to a porous structure in the resulting membrane and that heat treatment causes larger pores to be split into several smaller pores.

It is observed that membrane permeability and salt separation change abruptly when the average pore radius is reduced to less than 20–22 Å originally or by subsequent heat treatment.

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