Hemodialysis Membrane Prepared from Cellulose/*N*-Methylmorpholine-*N*-Oxide Solution. III. The Relationship Between the Drying Condition of the Membrane and Its Permeation Behavior

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ABSTRACT: The effects of drying condition on the performance (ultrafiltration rate, diffusive solute permeability, and sieving) of hemodialysis membranes prepared from cellulose/*N*-methylmorpholine-*N*-oxide (NMMO) solution (NMMO membrane) and cellulose/cuprammonium solution (cuprammonium membrane; the referential membrane) were studied. The drying condition investigated was the glycerin concentration of the solution, which was used to substitute glycerin for the water in the membrane before the membrane was dried. A lower glycerin concentration in the solution brought about a lower reswelling degree (water content) in the dried membrane in pure water, which resulted in a drop in the performance of the as-cast membrane. The NMMO membrane had a high water content and a high membrane performance compared with the cuprammonium membrane when both the membranes were treated under the same drying condition. The differences in the performance between both membrane series is discussed on the basis of the results of the observation of the membrane morphology by scanning electron microscopy, the observation of the crystallinity of the membranes by wide-angle X-ray diffraction, and the estimation of the pore structure of the membranes. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1671–1681, 2003

Key words: membranes; morphology; structure

INTRODUCTION

Nowadays, polymer membranes have largely contributed to the development of medical treatments. Particularly, dialysis membranes have a very important position in renal failure therapy as artificial kidneys.[1,2] For this purpose, regenerated cellulose membranes prepared by the cuprammonium rayon method have been used. However, it has been pointed out that the conventional cellulose membrane has two major faults in comparison with synthetic polymer membranes. One of the faults is its poor blood compatibility, represented by complement activation.[3–5] This problem was improved by the grafting of polyethylene glycol[6,7] or the fixation of vitamin E[8] on the membrane surface. The other fault is its low performance in the removal of low-molecular-weight proteins, of which accumulation in a patient's body could cause complications. For example, the accumulation of β_2-microglobulin (β_2-MG; 11.8 kDa) brings about amyloidosis.[9] This lower permeability occurs because of the membrane structure. That is, the cellulose membrane has a homogeneous and dense structure depending on the membrane preparation method. One of the methods to improve the poor permeability is the introduction of an asymmetric structure to it such as a synthetic polymer membrane. Inamoto and colleagues studied the effect of the regeneration conditions of the cuprammonium rayon method on the membrane structure and succeeded in preparing a cellulose membrane with an asymmetric structure and a high performance.[10,11] Another way to obtain an asymmetric structure would be to change the solvent from the cuprammonium solution to an organic solvent because it is expected that the membrane can form via a simple coagulation mechanism similar to that of synthetic polymer membranes.[12] In this viewpoint, *N*-methylmorpholine-*N*-oxide (NMMO) is attractive because of its strong dissolving power for cellulose, and the applications of the solvent to the manufacture of cellulosic products such as fiber and film (the NMMO method) have been investigated.[13–15] Indeed, regenerated cellulose fiber produced by the NMMO method was industrialized,[16] and a lot of studies on the manufacturing and characterization of the fiber have been carried out.[17–19] Such studies on the NMMO method interested us, and we investigated the applicability of

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this method to the preparation of a hemodialysis membrane with a high membrane performance. In previous articles,[20,21] the relationships between the preparation conditions of the membrane (i.e., cellulose concentration of the casting solution, coagulant composition, and coagulant temperature) and the membrane performance were reported. We concluded in those articles that the membranes prepared from a cellulose/NMMO solution (NMMO membrane) had excellent permeability performances compared with the membranes from the cuprammonium solution (cuprammonium membrane) and that the predominant factor affecting the membrane performance was the cellulose concentration. However, these evaluations were carried out with the as-cast wet membrane, which had been never dried. Usually, a dialysis membrane is prepared by a phase-inversion method and the just-obtained membrane is wet because water is almost always used in the coagulant process and/or in the washing process. From the viewpoint of the production of the membrane module, the process of drying the wet as-cast or as-span membrane is necessary. However, the water in the membrane plays an important role in the retention of membrane performance. Drying a membrane sometimes causes a drastic drop in performance, which is well known experimentally by membrane researchers. This phenomenon is common in many types of hydrophilic membranes, such as reverse osmosis, ultrafiltration, and dialysis membranes. To avoid the drop in performance by drying the membrane, researchers have substituted a water-soluble, low-molecular substance for the water in the membranes. The study of this problem was first carried out by Vos and Burris. The reverse osmosis membrane[22] and, then, the drying method of the cellulose acetate membrane for ultrafiltration was investigated by van Oss and Bronson with glycerin or sodium dodecylsulfate.[23] In a hemodialysis membrane, glycerin has been used as the substance because of its nontoxicity and efficiency of maintaining the membrane performance. The general drying procedure is as follows: the as-cast (as-span) membrane is soaked in a glycerin aqueous solution, and then, the membrane is passed through a dry oven. These processes drastically affect the membrane performance. Therefore, it is very important to establish the drying conditions when the membrane is industrialized. Although drying a membrane is a very important process, as mentioned previously, there are few reports on this matter. In this article, we describe the effects of the substitution of glycerin for the water in regenerated cellulose membranes on their performance [ultrafiltration rate (UFR), diffusive solute permeability, and sieving performance] and discuss the difference of the performance between NMMO and cuprammonium membranes on the basis of the results of the observation of membrane morphology by scanning electron microscopy (SEM), the observation of the crystallinity of the membranes by wide-angle X-ray diffraction (WAXD), and the estimation of the pore structure of the membranes.

EXPERIMENTAL

Materials

The cellulose used was cotton linter containing over 98% cellulose, and it was purchased from Taihei Paper Manufacture Co., Ltd. (Tokyo). The NMMO was monohydrate, containing 13.3 wt % water (melting point = 72°C), and was supplied by Nippon Nyukazai Co., Ltd. (Tokyo). NaOH and H_2SO_4 were reagent grade and were purchased from Kanto Kagaku Co., Ltd. (Tokyo).

Preparation of the membranes

As-cast wet membranes

As reported in the previous articles,[20,21] two kinds of regenerated cellulose membranes were prepared from a cellulose/NNMO solution and from a cellulose/cuprammonium solution. The cellulose concentration in the casting solution was 8 wt % in both cases. In the NMMO method, the coagulant used was pure water, and its temperature was 5°C. In the cuprammonium rayon method, the coagulation of cellulose was carried out in a 3.5*N* NaOH aqueous solution at 26°C, and then, regeneration was carried out in 1 wt % H_2SO_4 aqueous solution at room temperature.

Dried membranes

The as-cast wet membranes were soaked in glycerin aqueous solutions with 5, 10, 15, and 20 wt % glycerin for 15 h. After the membranes were taken out of the solution and wiped with filter paper to remove the excess glycerin solution, the membranes were put into a dry-air oven at 110°C for 30 min to dry.

Water content in the membranes

The dried membrane containing glycerin was soaked in pure water at room temperature for 3 days and was then fully rinsed with pure water to remove glycerin in the membrane. The water-swelled membrane obtained was weighed (W_w). The water-swelled membrane was dried at 80°C *in vacuo* for 24 h, and the membrane was weighed (W_d). The water content of the membrane (H_w) is defined by the following eq. (1).

$$H_w(\text{wt \%}) = (W_w - W_d)/W_w \times 100 \qquad (1)$$

H_w was converted to the volume fraction content (H_x) with the values for the densities of water (0.997 g/cm^3) and cellulose (1.5198 g/cm^3).[24]

Evaluation of the membrane performance

The UFR, diffusive solute permeability, and sieving coefficient (SC) of the membranes were measured by the same method described in the previous articles.[20,21] The methods are briefly described next.

UFR

UFR was obtained according to eq. (2).

$$\text{UFR (mL/m}^2\text{ h mmHg)} = V/SP \qquad (2)$$

where V is the water flux (mL/h) experimentally obtained at 37°C, S is the effective membrane area (1.15×10^{-3} m^2), and P is the operation pressure (250 mmHg).

Diffusive solute permeability

The diffusive solute permeability of the membrane was measured at 37°C with three kinds of solute (urea, creatinine, and vitamin B_{12}). The apparent diffusive solute permeability (P_m) is defined by eq. (3) under the assumption that the boundary layer resistance on both sides of the membrane is negligible:

$$P_m(\text{cm/min}) = \{\text{In}[(\Delta C(t_1)/\Delta C(t_2))]/[S(1/V_a + 1/V_b)(t_2 - t_1)] \qquad (3)$$

where t_1 and t_2 are the sampling times (t_1 = 30 min and t_2 = 60 min for urea and creatinine; t_1 = 60 min and t_2 = 120 min for vitamin B_{12}), $\Delta C(t)$ is the difference between the solute concentrations of both of the cells at each sampling time, V_a and V_b are the solution volumes in each cell ($V_a = V_b$ = 65 cm^3), and S is the effective membrane area (9.07 cm^2). The solute concentrations of the solutions in both the cells were determined by the urease–indophenol method for urea, the Jaffé method for creatinine, and spectrophotometry at 360 nm for vitamin B_{12}.[21]

SC

The measurement of SC was carried out with a saline solution with 1 wt % dextran at 37°C under a 250-mmHg operation pressure.[20] The SC for a certain molecular weight (MW) of dextran was calculated according to eq. (4):

$$\text{SC} = C_1/C_2 \qquad (4)$$

where C_1 and C_2 are the dextran concentrations for each MW (weight-average MW = 1–100 kDa) in the permeated solution and the mother solution, respectively, and they were measured by gel permeation chromatography with a monodisperse pullulan as the standard of MW.

Observation of membrane morphology

The dried membrane was fully rinsed with pure water to remove glycerin in the membrane, and the water-swelled membrane was obtained. The wet membrane, as-cast or water-swelled, was dehydrated by soaking in 50, 70, 80, 90, 95, and 99 vol % ethanol aqueous solution and ethanol successively for 30 min each, and the membrane containing ethanol was immersed into liquid nitrogen. The frozen membrane was fractured in liquid nitrogen to obtain a cross-section of the membrane. The fractured membrane was soaked in ethanol, *t*-butanol/ethanol (50/50 v/v), and *t*-butanol successively for 30 min (two times) each to substitute alcohol for water in the membrane and was then freeze-dried *in vacuo* for 3 days. The origin of this method was reported by Fukuda et al.[25] After platinum was spattered onto the dry membrane, the top surface and the cross-section of the membrane were observed under a scanning electron microscope equipped with a field emission gun at an accelerated voltage of 3 kV (JSM-840F, Jeol, Ltd., Tokyo, Japan).

Estimation of the crystallinity of the cellulose membranes

WAXD was carried out with a X-ray diffractometer (RAD-rB, Rigaku Denki Co., Ltd., Tokyo, Japan) with a scintillation counter. The crystallinity (χ_c) of the cellulose membrane was estimated by Segal et al.'s method, as described by eq. (5):[26]

$$\chi_c(X) = [I(002) - I_{\text{am}}]/I(002) \times 100 \qquad (5)$$

where $I(002)$ ($2\theta = 21.7°$) and I_{am} ($2\theta = 16.0°$) are the intensities corresponding to the (002) plane of the cellulose crystal and amorphous regions, respectively. The membrane sample was prepared according to the same method described in the Observation of Membrane Morphology section.

Estimation of the pore structure of the membranes

The pore radius and the number of the membrane were calculated from the straight cylindrical capillary pore model. In this model, the pore radius and its number are estimated on the basis of the Hagen–Poisseuille equation; together, these equations are known as Guérout–Elford–Ferry formula:[27]

$$J = N\pi\Delta P r^4 / 8\eta\Delta X \quad (6)$$

$$\varepsilon = N\pi r^2 \quad (7)$$

In eq. (6), J is the water flow rate, N is the pore number, ΔP is the pressure drop across the membrane, r is the pore radius, η is the viscosity of pure water, and ΔX is the membrane thickness. In eq. (7), ε is the surface porosity of the membrane.

RESULTS AND DISCUSSION

Water content in the membranes

It is well known that drying an as-cast hydrophilic hemodialysis membrane brings about a drop in its performance, as mentioned in the Introduction. To prevent a drop in the membrane performance in the drying process, the substitution of glycerin for the water in the membrane was carried out. From this, we believed that the degree of the glycerin substitution would determine the magnitude of the drop in the membrane performance. However, the absolute degree of the substitution could not be obtained because the state of perfect substitution cannot be defined. Therefore, it would be difficult to evaluate the degree of retention of the membrane performance as a function of the glycerin substitution degree quantitatively. If the drop in the performance due to the drying process is caused by the irreversible tightening of the membrane structure or the network structure of the polymer molecules, the drop would reflected by the reswelling degree of water (water content) of the membrane. Consequently, first, the relationship between the water content of the dried membrane and the glycerin concentration in the solution is discussed, where the glycerin solution was the one used for the substitution of glycerin for the water. The results shown in Figure 1 showed that the water content in both the membranes (NMMO and cuprammonium membranes) increased linearly with increasing glycerin concentration and, finally, seemed to be equal to the contents of the as-cast membranes. The two lines had significantly different gradients. The gradient of line of the NMMO membrane was larger than that of the cuprammonium membrane, and they crossed at about 10 wt % glycerin concentration. In the range over this concentration, the water content in NMMO membrane was higher than that of the latter membrane. From the comparison of the water contents of both of the membranes, we suggest that the as-cast NMMO membrane had a looser and weaker network structure of cellulose molecules, which implies that the performance of NMMO membrane was strongly affected by the drying condition, glycerin concentration.

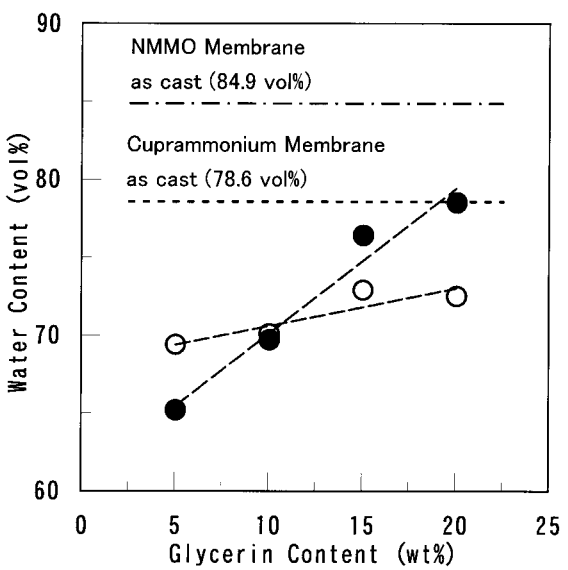

Figure 1 Effect of drying condition on the water content in the membranes: (●) NMMO and (○) cuprammonium membranes.

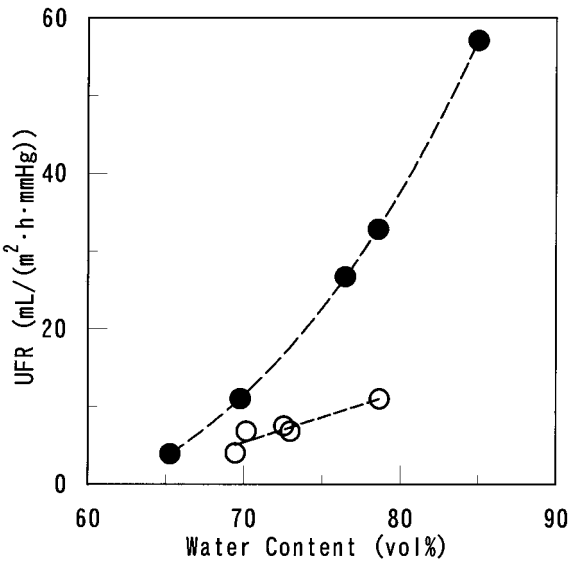

Figure 2 Effect of the water content in the membranes on UFR: (●) NMMO and (○) cuprammonium membranes.

UFR

UFR is one of the most important measurement of membrane performances. Figure 2 shows the relationship between the water content in the membranes and their UFRs for pure water. The UFRs of both of the membrane series increased with increasing water content, whereas they came close to the same value when the water content was less than 65 vol %. The UFR of the NMMO membrane drastically increased by fourteenfold (from 4 to 57 mL/m^2 · h · mmHg) with an increase in the water content from 65 to 85 vol %,

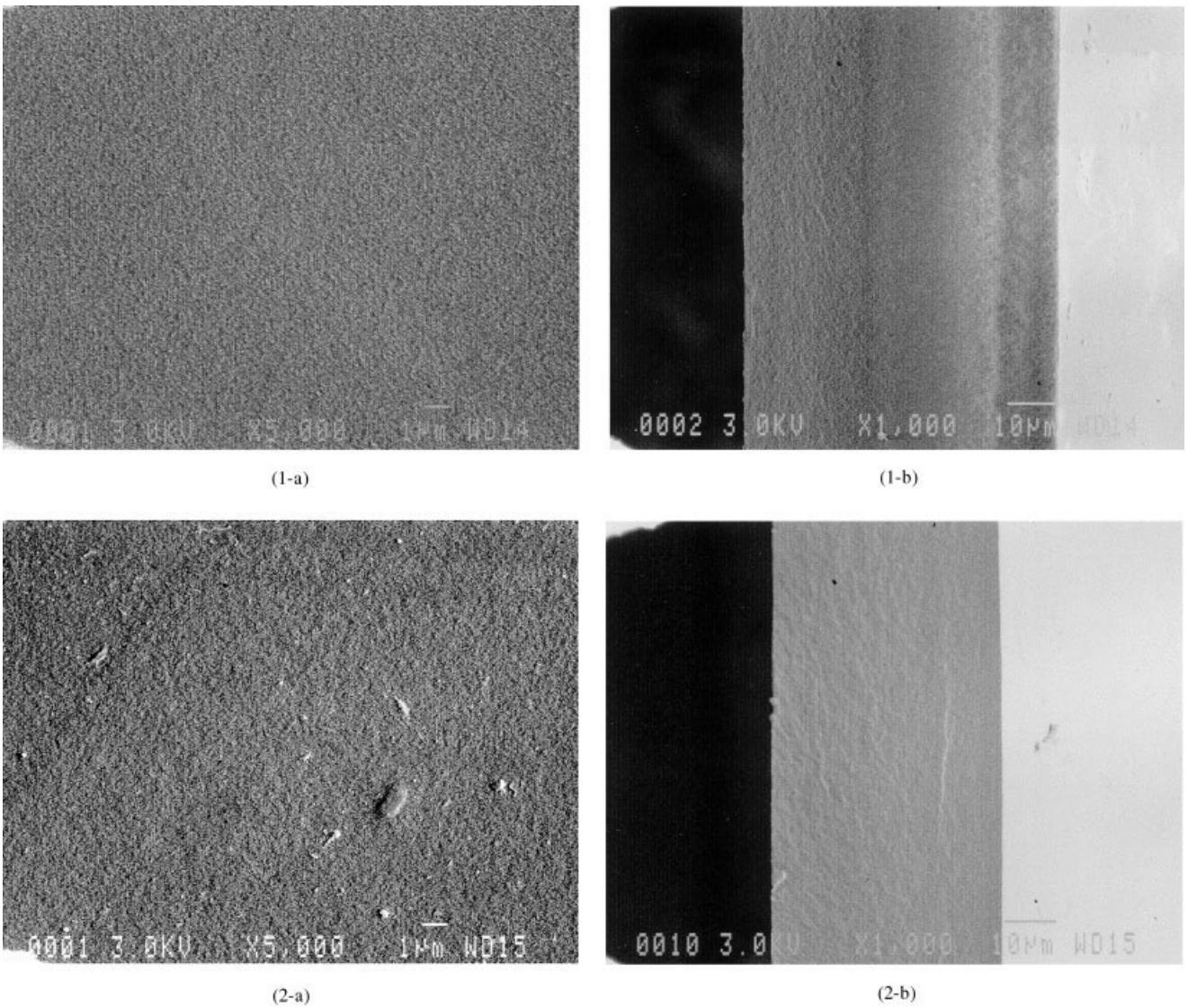

Figure 3 SEM micrographs of NMMO membranes. (1) As-cast membrane: (1-a) top surface (air side) and (1-b) cross-section (the right is the air side). (2) Dried membrane with 5 wt % glycerin aqueous solution: (2-a) top surface (air side) and (2-b) cross-section (the right is the air side).

whereas the increase in the UFR of cuprammonium membrane was small (from 4 to 9 $mL/m^2 \cdot h \cdot mmHg$). The increase in the UFR in each membrane series was attributed to the increase in the water content, but the difference between the UFR behaviors in both of the membrane series could not be explained only by the water content. To understand the reason for the difference, characterization of the membrane structures was carried out with SEM, WAXD, and estimation of pore structure. Effects of these factors on the membrane performance are described next.

Membrane morphology

Analysis of the surface pore structure or the membrane structure affecting the membrane performance is very important in designing a membrane. However, there have been no reports on the observation of the pores in dialysis membranes by direct methods such as electron microscopy. Dialysis membranes are, therefore, referred to as nonporous membranes. In a previous article,[21] we demonstrated that as-cast membranes prepared by NMMO and cuprammonium methods had nonporous structures on the basis of the results obtained from SEM observation. As the UFR was strongly influenced by the drying condition, especially in the NMMO membrane as described previously, a structural change in the membrane might have occurred. To confirm whether a structural change in the drying process could be observed by a direct method, the top surface and the cross-section of both of the membranes were observed with SEM.

Figures 3 and 4 are typical SEM micrographs of NMMO and cuprammonium membranes [Figs. 3(a)

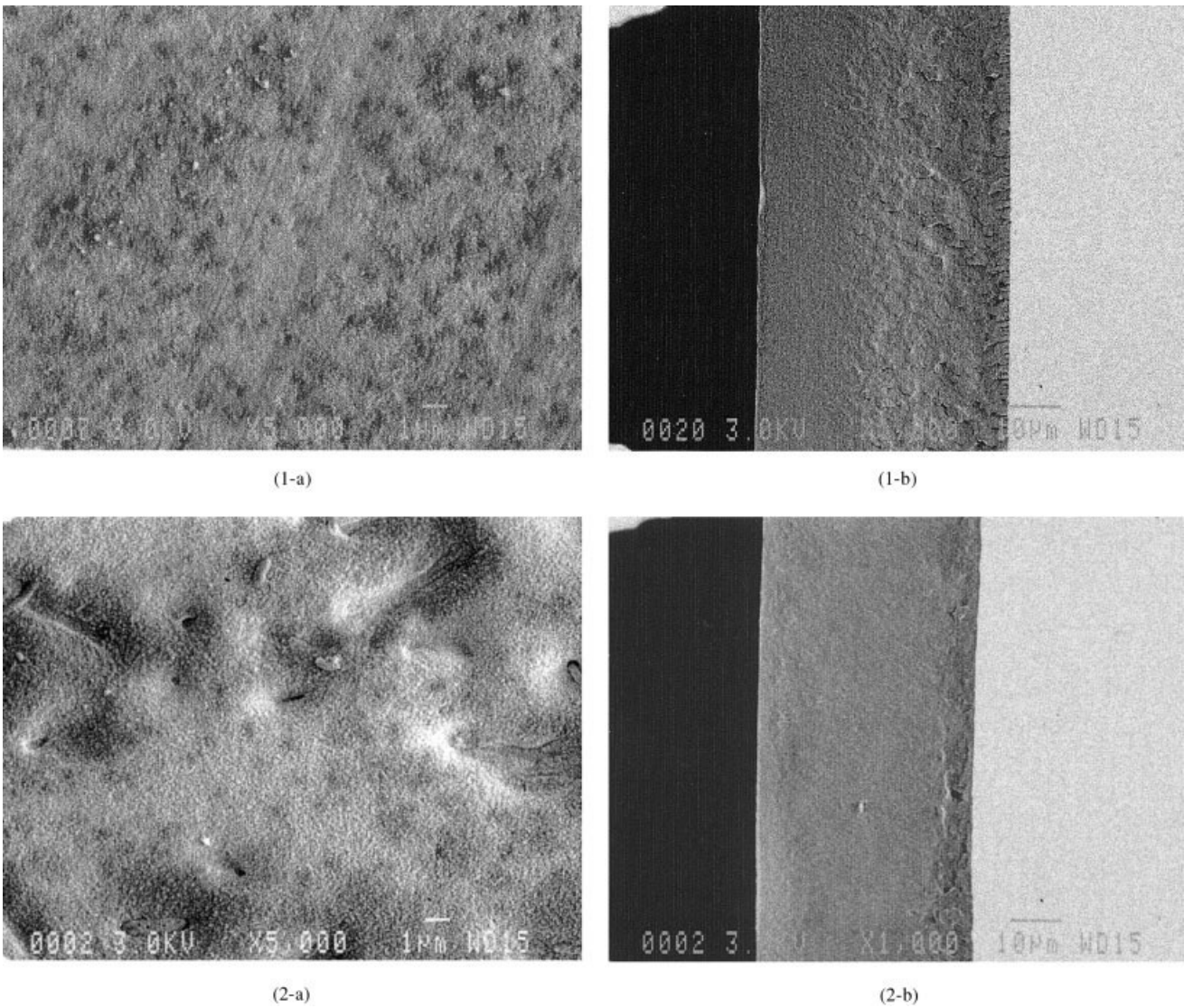

Figure 4 SEM micrographs of cuprammonium membranes. (1) As-cast membrane: (1-a) top surface (air side) and (1-b) cross-section (the right is the air side). (2) Dried membrane with 5 wt % glycerin aqueous solution: (2-a) top surface (air side) and (2-b) cross-section (the right is the air side).

and 4(a) show the top surface and Figs. 3(b) and 4(b) show the cross-section], respectively. Observed were the as-cast membrane [Figs. 3(1-a,1-b) and Fig. 4(1-a,1-b)] and the membrane dried with a 5 wt % glycerin solution [Figs. 3(2-a,2-b) and Fig. 4(2-a,2-b)]. This drying condition brought about the largest decrease in the UFR of both of the membranes. The cross-section images of the as-cast membranes and the dried membranes indicated that the NMMO and cuprammonium membranes had homogeneous and dense structures, and the images of the membrane surface in both of the series showed that there was no pore at the top surface. Quite similar images were also obtained for the membranes dried under other conditions (different concentrations of glycerin). From these results, we concluded that both of the membranes could be classified as nonporous, and there was no structural change before or after the drying the membrane via the substitution of glycerin. Therefore, it was difficult to explain the marked decrease in the UFR of the NMMO membrane from the viewpoint of the structural change observed by the direct method. In addition, the difference in the UFR between the NMMO and cuprammonium membranes also could not be explained by the SEM results.

Crystallinity of the cellulose membranes

The difference in the crystallinity between the NMMO and cuprammonium membranes were considered one of the factors affecting the permeation behaviors because these membranes were nonporous homogeneous membranes. Thus, the crystallinities of the membranes were investigated by WAXD. The repre-

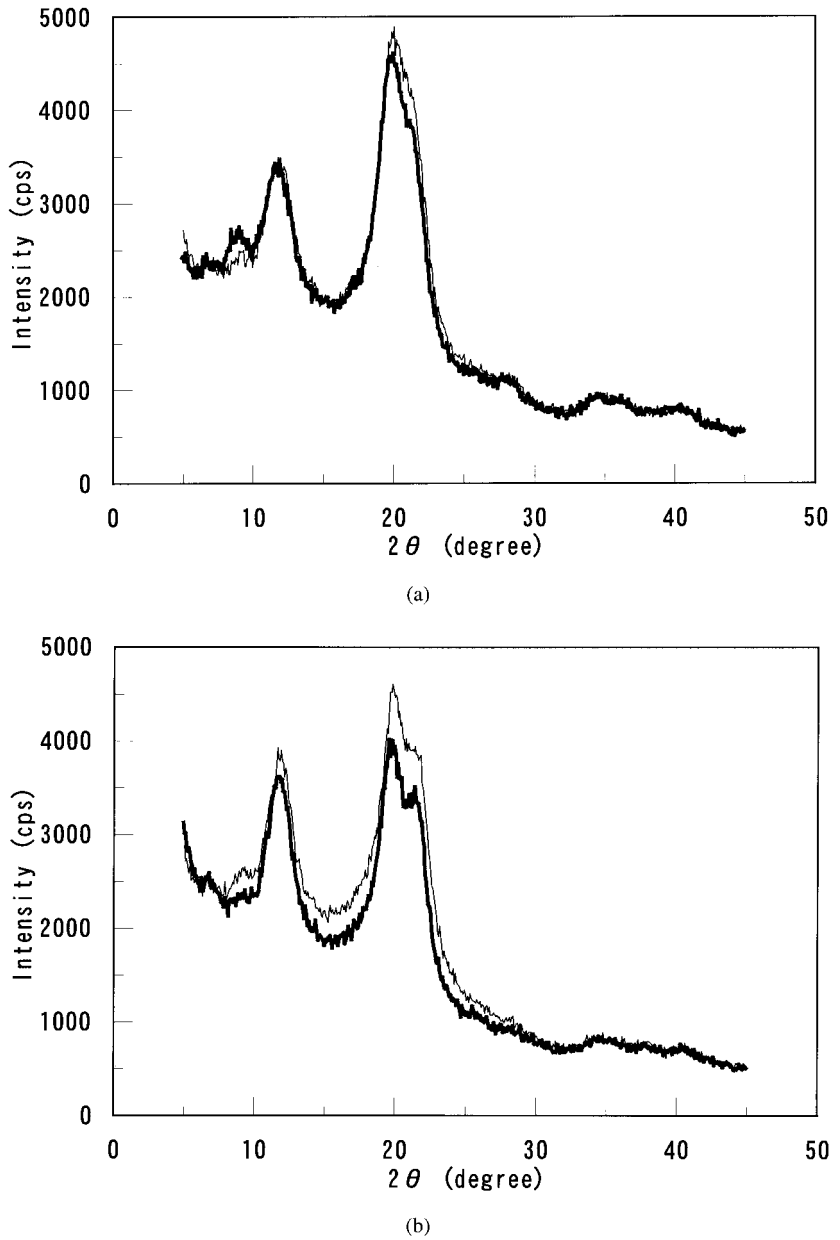

Figure 5 X-ray diffraction patterns of NMMO and cuprammonium membranes. (a) NMMO membranes: (—) as cast and (—) dried with a 5 wt % glycerin aqueous solution. (b) Cuprammonium membranes: (—) as cast and (—) dried with a 5 wt % glycerin aqueous solution.

sentative diffraction patterns of the NMMO and cuprammonium membranes are shown in Figure 5(a,b). In both of the membrane series, quite similar diffraction patterns were obtained for the dried membranes with 5 wt % glycerin solution. These results indicated that the crystalline structures of cellulose in the NMMO and cuprammonium membranes were cellulose II type. It is known that the cellulose regenerated from cuprammonium solution has a cellulose II type structure. In the case of cellulose regenerated from NMMO solution, different results were reported: one study reported that the cellulose had a type II structure,[28] and the other study reported that the cellulose had a type III structure.[29] On the basis of the diffraction patterns, the crystallinities in the membranes were estimated by Segal's method. The results are listed in Table I. The crystallinity in both of the membrane series were affected little by the drying condition (glycerin concentration of the solution in the drying process). Namely, the crystallization hardly proceeded in the drying process. Moreover, the crystallinity of the NMMO membrane was slightly smaller compared with that of the cuprammonium membrane. From these results, we concluded that the crystallinity of the membrane was not the main factor determining the difference in the UFR behavior of the membranes.

TABLE I
Characteristics of the Membranes

Membrane	Concentration of glycerin (wt %)	H_w (vol %)	UFR (mL/m^2 h mmHg)	Crystallinity (%)
NMMO	As-cast	84.9	57.1	43.8
	5	65.2	3.9	43.5
Cuprammonium	As-cast	78.6	12.2	46.1
	5	69.4	4.0	48.0

From the results of the morphological structure and crystallinity of the membranes, we deduced that the amorphous region or the network structure of molecular cellulose in the membrane was an important factor governing its performance. That is, the difference in the network structure between the NMMO and cuprammonium membrane series were a predominant factor causing the different membrane performance.

Pore structure of the membranes

As mentioned previously, the NMMO and cuprammonium membranes had nonporous structures, and we could not find the significant structural differences between them under SEM observation and through WAXD analysis. To explain the permeation behavior of a nonporous membrane, many indirect methods have been proposed to estimate the pore size and number of the membrane. These proposals were summarized by Sarbolouki[30] and Sakai.[31] These methods are classified into two groups. One is based on the water-flow properties of a membrane, and the other is based on the separation properties of a membrane with regard to a solute of known size. To deduce the reason for the difference in performance between the NMMO and cuprammonium membranes, it was valid to analyze the membrane pore structure (average pore radius and pore number) obtained from an indirect method. In this work, we adopted the simplest model of the former methods, which is known as Guérout–Elford–Ferry model. In this model, it is supposed that the membrane voids are comprised of straight cylindrical pores that are perpendicular to the membrane surface and that the hydraulic flux obeys the Poisseuille law. The calculation results, the pore radii, and the pore numbers of the membranes are shown in Figures 6 and 7. With increasing water content of the membranes, the pore radii of the membranes increased from 2.2 to 7.8 nm for the NMMO membrane and from 2.0 to 3.5 nm for the cuprammonium membrane. In addition, the water content strongly influenced the pore radius of the NMMO membrane as compared with that of the cuprammonium membrane. However, the pore number in both of the membrane series decreased linearly with increasing water content, and the pore number of the NMMO membrane was smaller than that of the cuprammonium membrane within the whole range of the water content investigated. From these results, we concluded that the difference between both the UFR behaviors was caused by the difference in the pore radii rather than that in the pore numbers; that is, the larger pore in the NMMO membrane brought about higher UFRs. In Figures 6 and 7, one can see that the pore structure of the NMMO membrane was strongly affected by the drying condition (glycerin concentration). This implies that a loose and weak network structure of molecular cellulose was formed in the regeneration process of the NMMO method.

Diffusive solute permeability

The removal of toxic low-molecular substances from the blood of a patient is the most important function of a hemodialysis membrane. To investigate the dialysis performance, urea (MW = 60) and creatinine (MW = 113) were used as representatives of such substances. In addition, to evaluate the performance, it is

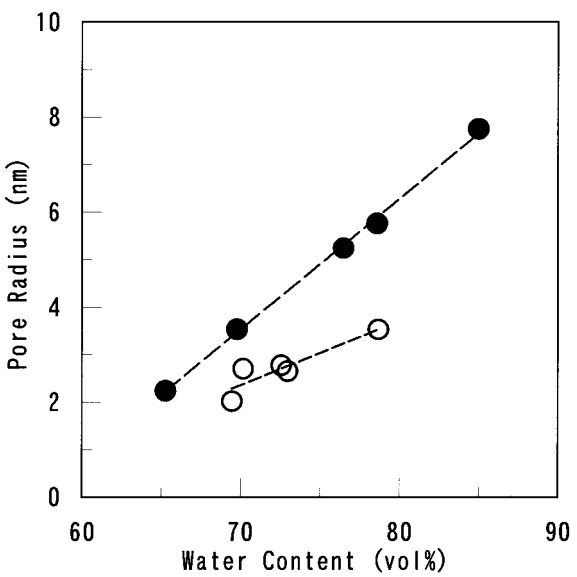

Figure 6 Relationship between the pore radius of the membrane and the water content in the membrane: (●) NMMO and (○) cuprammonium membranes.

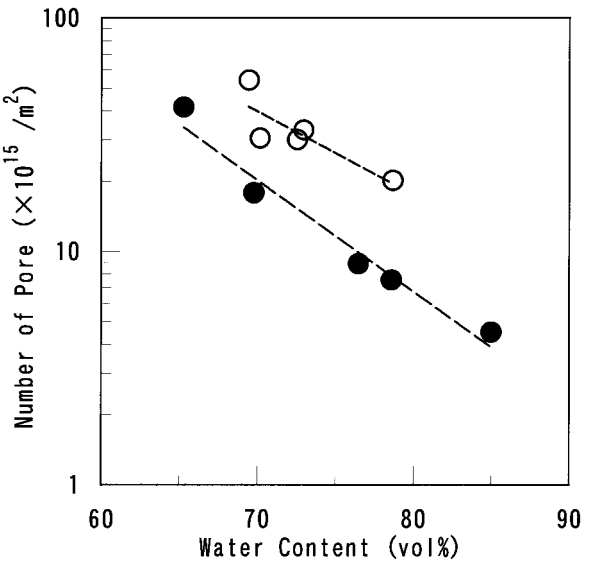

Figure 7 Relationship between the number of pores in the membrane and the water content in the membrane: (●) NMMO and (○) cuprammonium membranes.

very common to measure the diffusive permeability of a middle-MW substance. For this purpose, vitamin B_{12} (MW = 1355) has been used as the reference substance by many researchers. Thus, we measured the permeabilities of urea, creatinine, and vitamin B_{12}. The results are plotted against the water content of the membranes in Figure 8. This figure exhibits the following: (1) the permeabilities of these three solutes for both of the membranes increased linearly with increasing water content of the membranes, and (2) the diffusive permeability of the NMMO membrane was larger than that of the cuprammonium membrane, and the difference in the permeabilities between the NMMO and cuprammonium membranes apparently decreased with increasing solute molecular size. The first (no. 1) was explained by the increase in the pore volume in the membrane occupied with water through which the solute could diffuse. The second (no. 2) depended on the difference in the membrane pore structures. The factors affecting the diffusive permeability were the pore size and the pore number. On the basis of the aforementioned pore structure in both of the membrane series, we concluded that these permeation behaviors were predominantly governed by the difference in the pore size.

Sieving performance

It is known that a patient's blood contains an excess amount of low-MW proteins that are responsible for some of chronic side diseases. A typical example of these proteins is β_2-MG (MW = 11.8 kDa), and its accumulation in the body causes carpal tunnel syndrome.[9] These proteins cannot be removed efficiently through a hemodialysis membrane by diffusive permeation, but this can be done well by ultrafiltration. Therefore, the ultrafiltration performance in hemodialysis membranes is important. From this viewpoint, we evaluated the sieving performance of both of the membranes by determining the SC of dextran with a MW in the range 1–100 kDa. The results for the NMMO and cuprammonium membranes are shown in Figure 9(a,b). In an ideal hemodialysis membrane, the preferable SC at 10 kDa will be 1, and the SC at 100 kDa will be 0. Deviation from these ideal values means a low sieving performance. Particularly, a large SC over 0.05 at 100 kDa is a decisive defect for a hemodialysis membrane because it means the leakage of the valuable proteins such as albumin (MW = 66,000). In the NMMO membrane [Fig. 9 (a)], the concentration of glycerin solution used in the drying process strongly affected the sieving performance. The SC of the as-cast NMMO membrane at 100 kDa was about 0.2, which indicated that the sieving performance in the high-MW region was not satisfactory. However, in the dried NMMO membranes, the SCs at the same MW (100 kDa) were almost 0 (the ideal value) regardless of the drying condition or the water content, which indicated that these membranes would have ideal sieving performance for high-MW substances. The SC at 10 kDa decreased sharply from 0.88 to 0.22 with decreasing water content from 85 vol % (the as-cast membrane) to 65 vol %. This result revealed that drying should be carried out under the high glycerin concentration. That the sieving performance behaviors depended on the glycerin concentration could be ex-

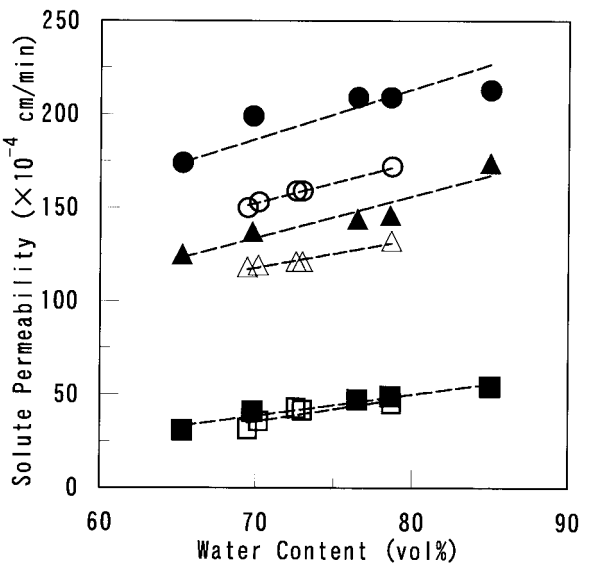

Figure 8 Relationship between the diffusive solute permeability and the water content in the membrane. NMMO membrane: (●) urea, (▲) creatinine, and (■) vitamin B_{12}. Cuprammonium membrane: (○) urea, (△) creatinine, and (□) vitamin B_{12}.

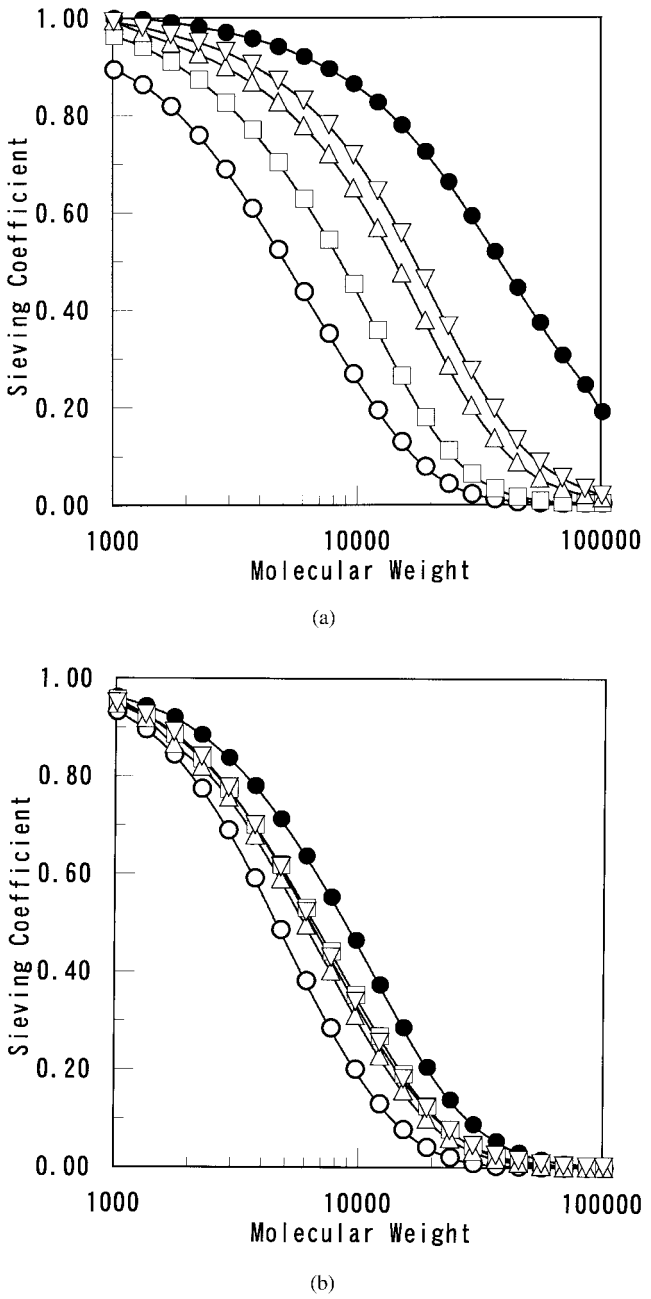

Figure 9 SC curves of the membranes. (a) NMMO and (b) cuprammonium membrane. (●) as-cast membrane and the membranes dried with glycerin aqueous solution with glycerin concentrations of (○) 5, (□) 10, (△) 15, and (▽) 20 wt %.

plained by the previously described speculation that the loose network structure was formed in the coagulation of the cellulose/NMMO solution and the reduction of the pore radius or the shrink of the network structure occurred in drying process. In the cuprammonium membrane [Fig. 9 (b)], the influence of the drying condition on the SC was markedly small compared with the NMMO membrane. The SC at 100 kDa was almost 0 for all of the cuprammonium membranes including the as-cast one. The SC at 10 kDa decreased from 0.48 to 0.18 with decreasing water content from 79 vol % (as-cast membrane) to 69 vol %, which meant insufficient sieving performance even for the as-cast membrane. These facts implied that in the cuprammonium membrane, the network structure of cellulose molecules formed during the regeneration was tight so that the drying process had little effect on the performance. This speculation was supported by the water content of the cuprammonium membrane, which was in a narrow range, 69–79 vol %, regardless of the drying condition, whereas that of NMMO membrane was in a wide range, 65–85 vol %.

To clarify the speculation on the network structure of the membrane, detailed analyses of both of the membranes by detailed X-ray diffraction analysis and dynamic viscoelastic analysis are now under investigation, and the results will be reported in the future.

CONCLUSIONS

The effect of drying condition on the performance of the NMMO membrane (i.e., UFR, diffusive solute permeability, and SC) was studied together with the cuprammonium membrane as a reference. The drying condition investigated was the glycerin concentration in the solution that was used to substitute glycerin for the water in the as-cast membrane. The reswelling degree of the dried NMMO membrane in pure water (water content) was more strongly affected by the glycerin concentration than that of the cuprammonium membrane. In addition, the membrane performances were strongly affected by the water content in the membrane. The diffusive solute permeabilities of urea, creatinine, and vitamin B_{12} for the NMMO membrane were higher than those for the cuprammonium membrane. The ultrafiltration performance of the membrane was measured in terms of SC. The SC of the NMMO membrane was strongly affected by the drying condition (glycerin concentration in the solution) as compared with cuprammonium membrane. These results mean that the choice of drying condition is very important for avoiding a drop in the membrane performance and that preferable performance properties can be given to the NMMO membrane by control of the glycerin concentration, whereas the cuprammonium membrane had poor performance regardless of the drying condition. SEM observation revealed that both the membranes were nonporous membranes and that there was no structural difference between the NMMO and cuprammonium membranes. WAXD analysis showed that the crystallinity had little effect on the membrane performance. The pore size and the pore number of the membrane were calculated according to the cylindrical capillary model. The results showed that the NMMO membrane had a larger pore radius and a smaller pore number than the cuprammonium membrane. These different pore features ex-

plained the difference in the permeation behaviors between both of the membrane series well.

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