Hemodialysis Membrane Prepared from Cellulose/*N*-Methylmorpholine-*N*-oxide Solution. II. Comparative Studies on the Permeation Characteristics of Membranes Prepared from *N*-Methylmorpholine-*N*-oxide and Cuprammonium Solutions

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Received 15 December 2001; accepted 26 August 2002

ABSTRACT: Two kinds of regenerated cellulose membranes for hemodialysis were prepared from casting solutions of *N*-methylmorpholine-*N*-oxide (NMMO) and cuprammonium (denoted NMMO membranes and cuprammonium membranes, respectively). The concentration of cellulose in the casting solution investigated was 6–8 wt %. The permeation characteristics of both membrane series were compared in terms of the ultrafiltration rate (UFR) of pure water, the sieving coefficient (SC) of dextran, and the solute permeabilities of urea, creatinine, and vitamin B_{12}. The UFR and SC of the NMMO membranes were strongly affected by the cellulose concentration of the casting solution, and NMMO was a preferable solvent for the production of cellulose membranes with high performance; the cuprammonium solution gave low-performance membranes. The pore structures of both types of membranes were estimated with the Hagen–Poiseuille law. The results showed that the NMMO membranes had larger pore radius and smaller pore numbers than the cuprammonium membranes. The differences in the membrane pore structures led to the differences in the performance between the two membrane series. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 333–339, 2003

Key words: membranes; structure; morphology

INTRODUCTION

Polymer membrane technology has contributed to great advances in medical care. In particular, dialysis membranes have been applied to therapy for renal failure and have been used as artificial kidneys (hemodialysis therapy).[1,2] The regenerated cellulose membrane prepared with the cuprammonium rayon method was the first hemodialysis membrane made for practical use with good success, and it is still used. However, the conventional cellulose membrane has two major faults in comparison with membranes prepared from synthetic polymers such as cellulose triacetate and polysulfone. One is its poor blood compatibility, represented by complement activation occurring during extracorporeal circulation.[3–5] As a solution to this problem, many chemical modifications of the membrane surface have been proposed, and some of them have successfully been commercialized, such as the grafting of poly(ethylene glycol)[6,7] and the fixation of vitamin E.[8] The other is its low permeability for low molecular weight proteins. The excessive existence of certain proteins in blood causes many kinds of complications. For example, it is well known that the accumulation of β_2-microglobulin (β_2-MG; 11,800 Da) brings about amyloidosis.[9] The reason for the lower permeability of such substances is thought to be as follows. The conventional cellulose membrane has a homogeneous and dense structure in which the predominant permeation mechanism is diffusion, so the protein molecule is too large to permeate through the membrane. One of the methods of improving this poor permeability is the introduction of an asymmetric structure, such as a synthetic polymer membrane. Inamoto and coworkers[10,11] reported such an effort. They investigated the effect of the regeneration condition in the cuprammonium rayon method on the membrane structure, and they concluded that a membrane with an asymmetric structure could be prepared and would result in high performance. Another way of obtaining this asymmetric structure could be changing the solvent from the cuprammonium solution to an organic solvent because it is expected that the membrane can form via a simple coagulation mechanism like synthetic polymer membranes.[12]

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Journal of Applied Polymer Science, Vol. 89, 333–339 (2003)

When the cuprammonium rayon method is considered from the viewpoint of industry, it is not economical and ecological because it requires toxic chemical reagents, (cupric sulfate, ammonia, sulfuric acid, and sodium hydroxide) and the complicated manufacturing processes previously mentioned. For the simplification of the dissolution/regeneration processes of cellulose, many attempts to dissolve cellulose in organic solvents have been made. Some examples include dimethylacetamide/lithium chloride,[13] dimethylsulfoxide/formalin,[14] and alkylamine-*N*-oxides, such as *N*-methylmorpholine-*N*-oxide (NMMO).[15,16] Among these solvents, NMMO is the best because of its ability to dissolve cellulose. NMMO dissolves cellulose directly without the formation of a cellulose complex or derivative, whereas the other solvent systems make a complex with cellulose. In addition, NMMO provides environmentally friendly processes.[17,18] Recently, a regenerated cellulose fiber prepared from an NMMO solution has been commercialized by Courtauls (United Kingdom) as Tencel and by Lenzing AG (Austria) as Lyocell.[19] Along with this industrialization, much research on the manufacturing and characterization of the fiber has been carried out.[20–22] From these facts, we focus our attention on the applicability of a cellulose/NMMO solution to the preparation of the cellulose membrane and the probability of improving the membrane performance because cellulose can easily be regenerated from an NMMO solution via a simple mechanism such as a synthetic polymer.

In a previous article,[23] we reported the effect of coagulation conditions (coagulant temperature and composition) on the ultrafiltration rate (UFR) and sieving coefficient (SC) of a hemodialysis membrane prepared from an NMMO solution. We concluded that the NMMO solution had a possibility of producing a membrane with high performance when coagulation with low-temperature water was employed. In this study, we compare the permeability characteristics of membranes from NMMO solutions with those of membranes obtained from cuprammonium solutions, and we discuss the reason for the differences in the performance between the two types of membranes.

EXPERIMENTAL

Materials

The cellulose used in this study was cotton linter supplied by Taihei Paper Manufacture Co., Ltd. (Tokyo, Japan). The content of α-cellulose in the linter was over 97.5%. The viscosity of the cellulose/cupriethylenediamine solution (cellulose = 0.5 wt %) and the polymerization degree of cellulose were 7.3 cP and 1180, respectively. NMMO was a monohydrate containing 13.3 wt % water (melting point = 72°C), and was supplied by Nippon Nyukazai Co., Ltd. (Tokyo, Japan). *n*-Propyl gallate (PG), sodium *n*-dodecyl sulfate (SDS), a 25 wt % NH_3 aqueous solution, Na_2SO_3, $CuSO_4 \cdot Cu(OH)_2$, NaOH, and H_2SO_4 were-reagent grade and were purchased from Kanto Kagaku Co., Ltd. (Tokyo, Japan). PG is a polyphenolic antioxidant and protects the cellulose molecule from oxidative decomposition.

Preparation of the cellulose solutions (casting solutions)

Two kinds of cellulose solutions were prepared according to the following procedures.

Cellulose/NMMO solution (NMMO solution)

After a mixture of NMMO, PG, and SDS became homogeneous and transparent at 90°C, cotton linter was added to the solution. The concentrations of PG and SDS were 0.25 wt % based on the weight of cellulose. The mixture was stirred at 90°C for 15 h with a mechanical stirrer. The obtained solution was filtered through two stainless filters, the apertures of which were 100 and 10 μm. Therefore, solutions containing 6, 7, and 8 wt % cellulose were obtained.

Cellulose/cuprammonium solution (cuprammonium solution)

A cuprammonium hydroxide aqueous solution was prepared from $CuSO_4 \cdot Cu(OH)_2$, a 10 wt % Na_2SO_3 aqueous solution, and a 25 wt % NH_3 aqueous solution. After cotton linter was added to the cuprammonium solution, a 10 wt % NaOH aqueous solution was added by degrees. The mixture was stirred mechanically at 10°C for 8 h. The obtained solution was filtered through the same filters mentioned earlier. Therefore, solutions containing 6 and 8 wt % cellulose were obtained. The molar ratio of cellulose to Cu to NH_3 in the solutions was 1.00/0.47/9.37.

Preparation of the regenerated cellulose membranes

NMMO membrane (membrane prepared from an NMMO solution)

An NMMO solution was cast onto a glass plate at 90°C with a doctor blade with clearances of 100–300 μm. The glass plate was immersed immediately into 1 L of deionized water (coagulant) at 5°C for 1 h, and then the membrane formed was washed thoroughly. The obtained membrane was never dried in this work, and the thickness of the wet membranes was 48–68 μm.

Cuprammonium membrane (membrane prepared from a cuprammonium solution)

A cuprammonium solution was cast onto a glass plate at room temperature by the same method mentioned previously. The glass plate first was immersed into a coagulation bath (1 L) of a 3.5*N* NaOH aqueous solution at 26°C for 30 min and rinsed with deionized water at room temperature for 15 min. The glass plate then was immersed into a regeneration bath (1 L) of a 1 wt % H_2SO_4 aqueous solution at room temperature for 30 min and rinsed with deionized water. The obtained membrane was never dried in this work, and the thickness of the wet membrane was 60–63 μm.

Water content in the membranes

The wet membrane kept in pure water was weighed quickly after excessive water on the membrane surface was wiped with filter paper. The weight of the dry membrane was measured after the wet membrane was dried at 80°C for 24 h *in vacuo*. The water content in the membrane is defined as follows:

$$\text{Water Content (vol\%)} = [(W_{\text{wet}} - W_{\text{dry}})/\rho_1] \div \{[(W_{\text{wet}} - W_{\text{dry}})]/\rho_1] + (W_{\text{dry}}/\rho_2)\} \times 100 \quad (1)$$

where W_{wet} and W_{dry} are the weights of the wet and the dry membranes, respectively, and ρ_1 and ρ_2 are the densities of water (0.997 g/cm^3 at 25°C) and cellulose (1.519 g/cm^3),[24] respectively.

Evaluation of the permeability characteristics of the membranes

UFR

UFR was measured at 37°C with an ultrafilter unit holder (UHP-43K, Advantec Toyo Co., Ltd., Tokyo, Japan). The UFR was calculated as follows:

$$\text{UFR}[\text{mL}/(\text{m}^2 \cdot \text{h} \cdot \text{mmHg})] = V/SP \quad (2)$$

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

SC

The SC of the membranes for dextran was determined with 1 wt % dextran in a saline solution. The membrane holder was the same one used for the UFR measurements. The dextran used was a mixture of Dextran T10 [weight-average molecular weight (M_w) = 10,000] and T40 (M_w = 40,000; Amersham Biosciences, K.K., Tokyo, Japan), and its composition (T10/T40) was 50:50 (w/w). The measurements were carried out at 37°C under 250 mmHg of operation pressure. The molecular weight and concentration of dextran in the permeate and permeant solutions were measured by gel permeation chromatography (GPC; Shodex GPC System 21, Showa Denko Co., Ltd., Tokyo, Japan) with two columns connected to each other (Shodex OHpak, KB-803, Showa Denko). In the GPC measurements, monodisperse pullulan supplied by Showa Denko (Shodex Standard P82) was used as a standard of the molecular weight. The SC at a certain molecular weight was calculated as follows:

$$(\text{SC}) = C_1/C_2 \quad (3)$$

where C_1 and C_2 are the dextran concentrations for a certain molecular weight (M_w = 1–100 kDa) in the permeate and permeant solutions, respectively.

Diffusive solute permeability

The diffusive solute permeability of a membrane was measured at 37°C with a membrane holder made of an acrylic resin, which was separated into two cells by the membrane. One of the cells was filled with pure deionized water, and the other was filled with an aqueous solution of a single solute (test solution). The solutes used were urea, creatinine, and vitamin B_{12}, and their initial concentrations in the test solutions were 100, 10, and 5 mg/dL, respectively. Creatinine (molecular weigh = 143) is one of the uric toxic substances produced by the metabolism of proteins or amino acids and is removed from blood to urine through glomerular. The media in both cells were stirred magnetically during the experiment. The mass transfers of urea and creatinine were followed for 60 min and that of vitamin B_{12} was followed for 120 min after the start of the measurement. The solute concentrations of the solutions in both cells were determined by the urease–indophenol method[25,26] (Urea Nitrogen B-Test Wako, Wako Pure Chemicals Co., Ltd., Osaka, Japan) for urea, the Jaffé method (Creatinine-Test Wako, Wako Pure Chemicals) for creatinine, and spectrophotometry at 360 nm for vitamin B_{12} with a spectrophotometer (U-2001, Hitachi Co., Ltd., Tokyo, Japan). The apparent diffusive solute permeability (P_m) was defined by eq. (4) under the assumption that the boundary layer resistance on both sides of the membrane was negligible:

$$P_m(\text{cm/min}) = \{\ln[(\Delta C(t_1)/\Delta C(t_2)]\}/[S(1/V_a + 1/V_b)(t_2 - t_1)] \quad (4)$$

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 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).

Observation of the membrane morphology

The wet membrane was dehydrated by being soaked in 50, 70, 80, 90, 95, and 99 vol % ethanol aqueous solutions and ethanol successively for 30 min each, and the membrane containing ethanol was immersed in liquid nitrogen. The frozen membrane was fractured in liquid nitrogen so that the cross section of the membrane could be obtained. The fractured membrane was soaked in ethanol, *t*-butanol/ethanol (50/50 vol %), and *t*-butanol successively for 30 min (two times) each to substitute alcohol for water in the membrane, and then it was freeze-dried *in vacuo* for 3 days. The origin of this method was the one reported by Fukuda et al.[27] After platinum was spattered onto the dry membrane, the top surface and cross section of the membrane were observed with a scanning electron microscopy (SEM) instrument equipped with a field emission gun at an accelerated voltage of 3 kV (JSM-840F, JEOL, Ltd., Tokyo, Japan).

Estimation of the membrane pore structure

The pore radius and its number were calculated with the Guérout–Elford–Ferry formula [eqs. (5) and (6)][28] based on the Hagen–Poiseuille law:

$$J = N\pi\Delta P r^4/8\eta\Delta X \tag{5}$$

$$\varepsilon = N\pi r^2 \tag{6}$$

where 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, ΔX is the membrane thickness, and ϵ is the surface porosity of the membrane.

RESULTS AND DISCUSSION

UFR performance

UFR, which is one of the most important performance characteristics for hemodialysis membranes, is first described. The effect of the cellulose concentration in the casting solution on the UFR of both membrane series was investigated. The results are shown in Figure 1, where UFR* is plotted against the cellulose concentration instead of UFR so that the influence of the membrane thickness on UFR will be cancelled. The UFRs of the NMMO membranes are markedly high in comparison with those of cuprammonium membranes. The increase in the cellulose concentration of the casting solution brings about a decrease in the UFRs of NMMO membranes significantly, whereas in cuprammonium membranes, the change in the cellulose concentration has little effect on the UFRs.

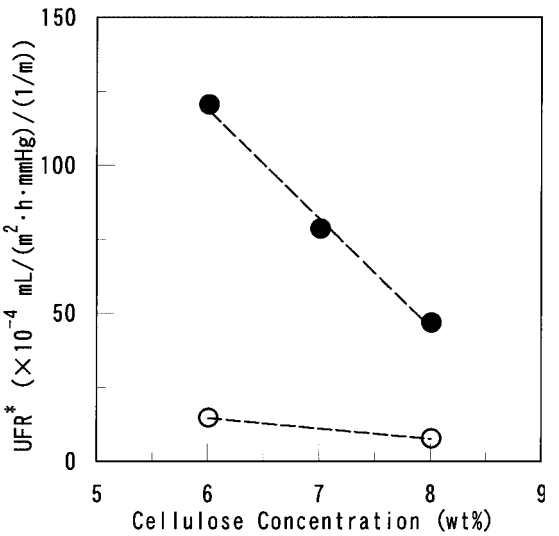

Figure 1 Dependence of UFR on the cellulose concentration of the casting solution: (●) NMMO membrane and (○) cuprammonium membrane. UFR* = UFR [mL/(m^2 h mmHg)] × membrane thickness (m).

Sieving performance

As described in the introduction, the selective removal of certain proteins in patient blood is important. That is, low molecular proteins such as β_2-MG (11.8 kDa) should be removed, whereas valuable middle or high molecular weight proteins such as albumin (66 kDa) should not. In general, it is well known that proteins cannot permeate through a membrane sufficiently by diffusion because of their large molecular size. Therefore, it is true that the ultrafiltration (sieving) performance for a substance with a molecular weight of 10–100 kDa is one of the most important characteristics for hemodialysis membranes. In this study, this performance was investigated from the viewpoint of the SC of dextran, together with the effect of the cellulose concentration of the casting solution on the SC. The SC curves of NMMO and cuprammonium membranes are shown in Figure 2. In the figure, SC = 1.00 means that the substance can permeate through the membrane without any resistance, and SC = 0 means that the substance cannot permeate through it at all. For NMMO membrane, the shape of the SC curve changed drastically according to the change in the cellulose concentration in the casting solution. The SCs at 10 kDa were high, over 0.85, regardless of the cellulose concentration, and the SC at 100 kDa decreased markedly from 0.84 to 0.19 with the increase in the cellulose concentration from 6 to 8 wt %. From these results, we can conclude that the casting solution

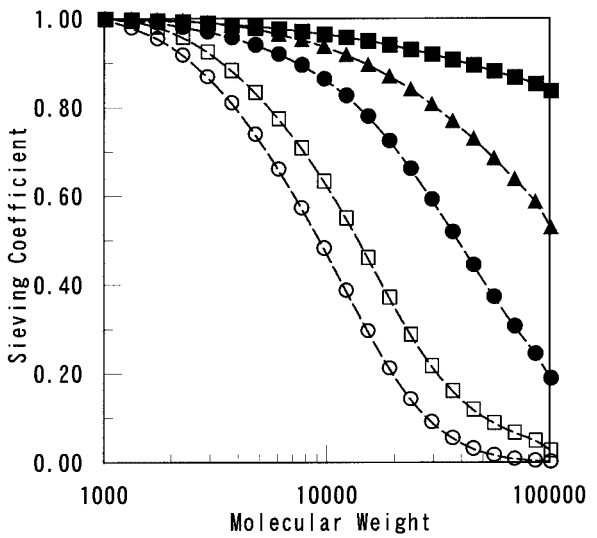

Figure 2 SC curves of the NMMO membranes (closed symbols) and cuprammonium membranes (open symbols) with the following cellulose concentrations in the casting solutions: (■,□) 6, (▲) 7, and (●,○) 8 wt %.

with 8 wt % cellulose gave a membrane with good performance. However, in the series of cuprammonium membranes, the cellulose concentration of the casting solution had little effect on the shape of the SC curves and values. The SCs at 10 and 100 kDa were about 0.5 and 0, respectively. These results show that the sieving performance of the cuprammonium membranes was not satisfactory because of the low SC at 10 kDa. Such SC curves of the cuprammonium membranes in this study express the typical sieving performance of conventional regenerated cellulose membranes.

Solute permeability

The removal of toxic low molecular weight substances, such as urea and creatinine, is a basic function of a hemodialysis membrane. Such substances can be removed by a diffusion mechanism. To evaluate the performance of the membranes, we investigated the diffusive solute permeability of urea, creatinine, and vitamin B_{12} with both membranes prepared from casting solutions containing 8 wt % cellulose; this gave a preferable sieving performance to the NMMO membranes. The results are shown in Figure 3. The diffusive solute permeability depended on the molecule size of the solute. That is, the higher the molecular weight was , the lower its solute permeability became. For urea and creatinine, the NMMO membranes gave a higher solute permeability than the cuprammonium membranes, whereas the permeability of vitamin B_{12} for both types of membranes was on the same level, about 50×10^{-4} cm/min.

Membrane morphology

The analysis of the surface pore structure or the membrane structure affecting the membrane performance is very important to the design of a membrane. There are, however, no reports on the observation of pores in reverse osmosis or dialysis membranes by direct methods such as electron microscopy. These membranes are, therefore, called nonporous membranes.

Figure 4 shows the morphologies (SEM micrographs) of NMMO and cuprammonium membranes from 8 wt % cellulose solutions. The top surfaces and cross sections of the membranes are shown in Figure 4 (a,b), respectively. The images of the top surfaces of both membranes indicate that these membranes had smooth surfaces and no porous structures. In the SEM micrograph of the top surface of the cuprammonium membrane, a dark spot can be observed. We, however, believe this phenomenon was due to the artifact because the morphology was not changed between the dark and bright parts. The SEM micrographs of the cross sections of the membranes show that both membranes had a dense and homogeneous structure in their cross sections. It is known that the membrane structure formed by alkaline coagulation in the cuprammonium rayon method is a dense structure.[29] Our result of cuprammonium membrane is in good agreement with this report. On the basis of these results, we conclude that the NMMO and cuprammonium membranes prepared from the casting solution with 8 wt % cellulose had the same structure and could be categorized as nonporous membranes. Consequently, the differences in the membrane perfor-

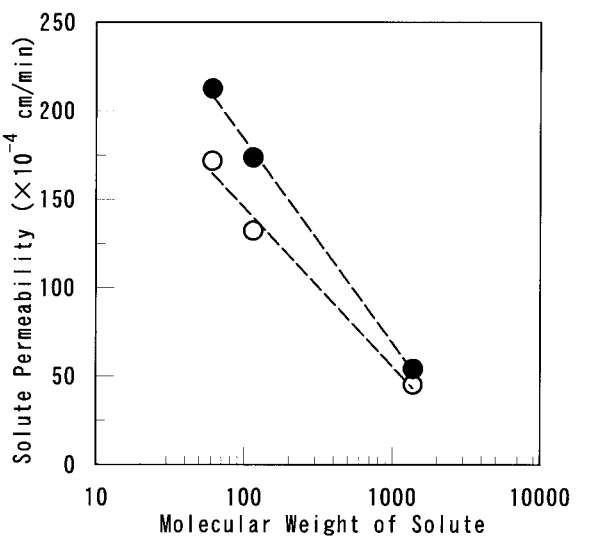

Figure 3 Relationship between the diffusive solute permeability and the molecular weight of the solute for (●) NMMO and (○) cuprammonium membranes with a cellulose concentration of 8 wt % in the casting solutions. The molecular weights were 60 for urea, 113 for creatinine, and 1,355 for vitamin B_{12}.

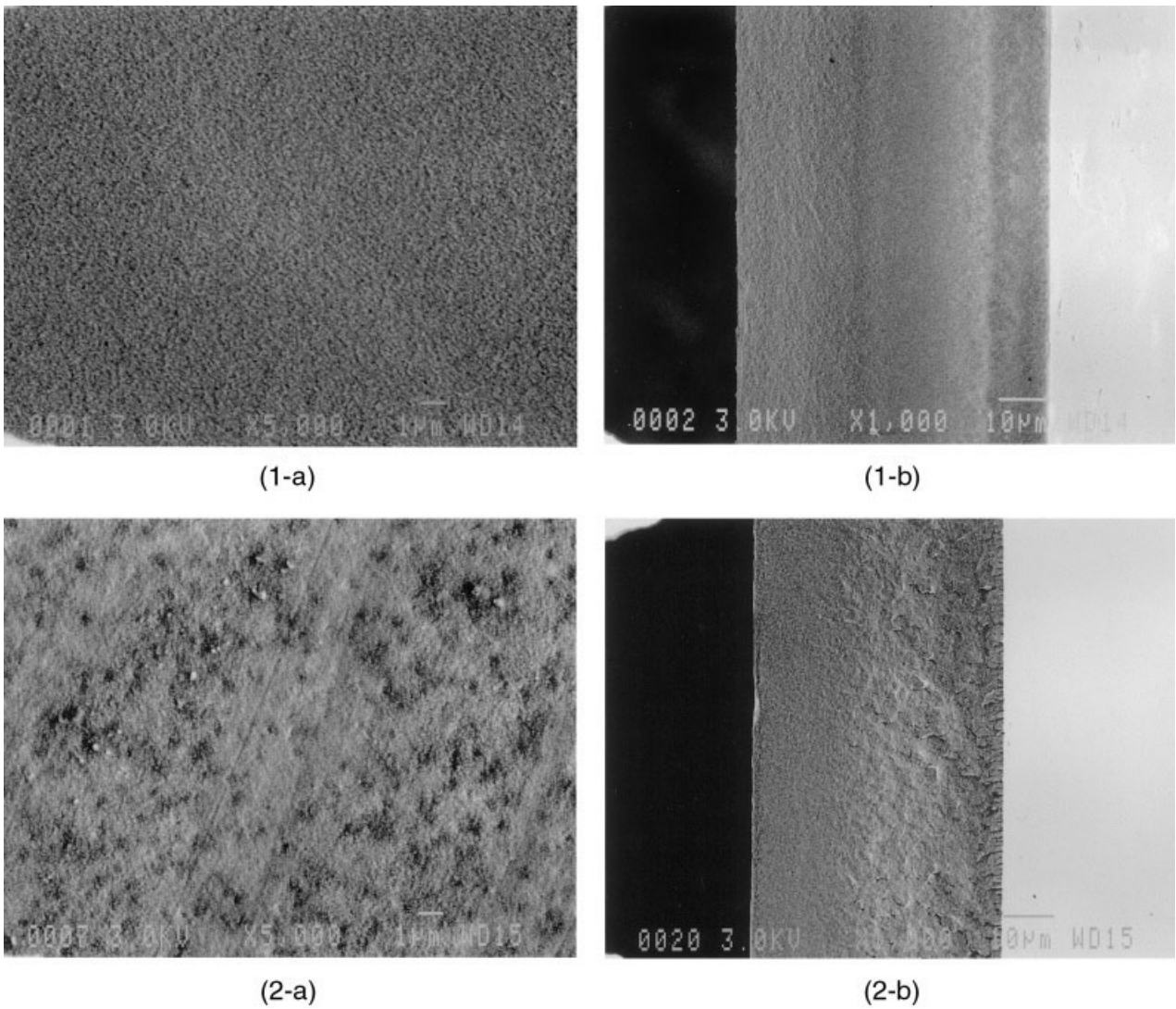

Figure 4 SEM micrographs of (1-a) the top surface (air side) and (1-b) the cross section (air side on the right) of the NMMO membrane and (2-a) the top surface (air side) and (2-b) cross section (air side on the right) of the cuprammonium membrane.

mance between the NMMO and cuprammonium membranes cannot be explained by the membrane structure observed by the direct method. Therefore, we further investigated the differences in performance.

Pore structure of the membranes

As previously mentioned, it is difficult to observe the pore structure by a direct method such as SEM. However, many indirect methods of estimating the pore size and number of nonporous membranes have been proposed. These methods were reviewed by Sarbolouki[30] and Sakai.[31] To deduce the reason for the differences in performance between NMMO and cuprammonium membranes, we analyzed the membrane pore structure (average pore radius and pore number) obtained from the hydraulic permeation theory. According to the Guérout–Elford–Ferry formula,[28] we estimated the pore structure for both membranes. The results are summarized in Table I, which shows that the pore radius of the NMMO membrane was about twice as large as that of the cuprammonium membrane and that the pore number of the NMMO membrane was smaller than that of the cuprammonium membrane. These results lead to the conclusion that the higher performances of the NMMO membranes in UFR, SC, and solute permeability were caused by the large pore size.

Further investigations, including the observation of the membrane surface morphology by atomic force microscopy and the analysis of the crystalline structure of the membrane by X-ray diffraction, are in progress and will be reported elsewhere.

CONCLUSIONS

The permeation characteristics of two kinds of dialysis membranes prepared from NMMO and cuprammo-

TABLE I
Characteristics of the Membranes

Membrane[a]	Thickness (μm)	UFR (mL/(m^2 h mmHg))	Swelling degree (vol %)	Pore radius[b] (nm)	Pore number[b] ($\times 10^{15}$/m^2)
NMMO	61	74.8	84.9	7.7	4.6
Cuprammonium	63	12.3	78.6	3.3	23.3

[a] Prepared from casting solution with 8 wt % cellulose.
[b] Calculated from the Guérout–Elford–Ferry formula.

nium solutions were investigated, with the cellulose concentration of the casting solution varied from 6 to 8 wt %. The UFR of the NMMO membrane was markedly high and depended strongly on the cellulose concentration of the casting solution with respect to that of the cuprammonium membrane. The sieving performance of the NMMO membrane was also strongly affected by the cellulose concentration, and the casting solution containing 8 wt % cellulose gave an excellent performance. However, for the cuprammonium membrane, the cellulose concentration in the casting solution had little effect on the sieving performance, and the performance was insufficient. As for diffusive solute permeability, the NMMO membrane was better than the cuprammonium membrane. SEM observations showed that both membranes had apparently the same structures, and they were classified as dense, nonporous membranes. To investigate the differences in the permeation behaviors between the two membranes, we estimated indirectly the pore structure of the membranes with the Guérout–Elford–Ferry formula. The calculations showed that the NMMO membrane had a larger pore radius and a smaller pore number than the cuprammonium membrane. From these results, we concluded that the larger pore size in the NMMO membrane caused its high performance.

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