Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Uragami, Tadashi , Sugitani, Yasuhiro and Sugihara, Mizuho(1982) 'Studies on Syntheses and Permeabilities of Special Polymer Membranes. 26. Preparation and Permeation Characteristics of Cellulose Membranes', Separation Science and Technology, 17: 2, 307 — 317
To link to this Article: DOI: 10.1080/01496398208068541
URL: http://dx.doi.org/10.1080/01496398208068541

SEPARATION SCIENCE AND TECHNOLOGY, 17(2), pp. 307-317, 1982

Studies on Syntheses and Permeabilities of Special Polymer Membranes. 26. Preparation and Permeation Characteristics of Cellulose Membranes

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Abstract

New preparation methods of cellulose membranes were studied. Homogeneous, strong cellulose membranes were obtained from mixtures of 1 to 3 g of cellulose, 5 to 10 g of paraformaldehyde, and 80 g of dimethylsulfoxide. The permeation characteristics and bursting strengths of these cellulose membranes were influenced significantly by preparation conditions of the membranes and permeation conditions; the former conditions included cellulose concentration and amount of paraformaldehyde in the casting mixture, temperatures of preparation, and heat treatment of the membranes; the latter, feed concentration. These results were attributed to structures of the resulting membranes. The permeation rates for aqueous solutions of poly(ethylene glycols) were greater than for pure water. This phenomenon was discussed from viewpoints of water structure. The permeability and bursting strength of a certain cellulose membrane prepared in this work were superior to those of cuprophane membranes.

INTRODUCTION

The membranes most commonly used at present in the artificial kidney are cellulose (prepared by the xanthate process) and cuprophane (prepared by the cuprammonium process). To improve the strengths of these membranes is to provide an advantage in handling. The membranes with modified

hydrophilic polymers, such as poly(vinyl alcohol), poly(vinyl pyrrolidone), and poly(2-hydroxyethyl metcrylate), have higher permeabilities than that of the cuprophane membrane, but the mechanical strengths of these membranes are rather small (*1–3*). On the other hand, when hydrophobic polymers are employed in order to improve the mechanical strength, well-defined pores in the membranes are required.

In general, the permeabilities and the mechanical strengths of membranes swollen with water are related to the hydrophilicity and hydrophobicity of the membrane material and the crystallinity of the membrane. From these viewpoints, many membranes are prepared by the blending and grafting of hydrophilic polymers with hydrophobic polymers (*4*) and by heat treatment (*3*), but the permeabilities and mechanical strengths of these membranes are inferior to those of the cuprophane membrane. Also, cellulose membranes which are hydrolyzed cellulose acetate (*5*) and cellulose nitrate (*6*) membranes do not have good mechanical strength or good separation characteristics.

Cellulose is a structural material in the wet state synthesized by the plant. The strength of cellulose in this state is very great. We took note of this point and attempted to prepare cellulose membranes by a new method. Recently, Johnson et al. (*7*) reported that a mixture of dimethylsulfoxide and paraformaldehyde was a very good solvent for cellulose. In this paper the preparation conditions of cellulose membranes using the above solvent and the characteristics of cellulose membranes obtained are studied in some detail. Also, the effect of the solute poly(ethylene glycol) on permeability through cellulose membranes is discussed from the viewpoint of water structure.

EXPERIMENTAL

Materials

Pulp flock cellulose powder (produced by Sanyo Kokusaku Pulp Co., w-4), which was dried under reduced pressure, was employed as the membrane substance. Dimethylsulfoxide (DMSO) and paraformaldehyde (PF), used for the preparation of membranes, were pure commercial reagents. Three kinds of poly(ethylene glycol) (supplied by Sanyo Kasei Co.), used as the solute of the feed solutions, were PEG 200, PEG 1000, and PEG 6000 whose number-average molecular weight were 190-210, 950-1050, and 7800-9000, respectively.

Preparation of Membranes

Cellulose powder immersed in DMSO was stirred in a stream of nitrogen gas for 3 h at 110°C. The desired amount of PF was subsequently added to this heterogeneous mixture and simultaneously the nitrogen gas was stopped. When this mixture was stirred for 90 min at 115°C, the cellulose powder dissolved. This solution was filtered at a desired temperature in an oven with gauze consisting of four layers to remove undecomposed PF. The membranes were made by pouring this clear filtrate (casting solution) onto a glass plate having a rim in an oven at a suitable temperature, for evaporation of the solvent in a desired period. The glass plate together with the solution was then immersed in water (25°C).

Apparatus and Measurements

The apparatus and the experimental procedure have been described in earlier papers (*8, 9*). Details of the experimental conditions are given in the figure captions.

RESULTS AND DISCUSSION

Adequate Conditions for Preparation of Membranes

The adequate conditions for preparation of cellulose membranes are summarized in Table 1. Here the DMSO content is kept constant at 80 g, and the content of cellulose and PF are changed. When the cellulose content is not more than 0.5 g, an entanglement between the cellulose molecules is small so that the concentration of cellulose in the casting solution is dilute. Therefore, the resulting membranes are very weak and heterogeneous. When 5 to 10 g of PF are added in the range of 1.0 to 2.5 g cellulose contents, the dissolved states of cellulose molecules are suitable, and consequently the membranes obtained are homogeneous, transparent, and strong. When the PF is 2.5 g, the cellulose molecules cannot be dissolved. However, this amount should suffice for the hydroxymethylation of cellulose molecules. This result suggests that the PF molecules are not decomposed effectively to formaldehyde. When the content is over 10 g, the dissolved states of cellulose molecules are better but the viscosities of casting solutions are very high. Therefore, it is very difficult to obtain homogeneous thin membranes. Consequently, the conditions within the frame in Table 1 are needed to obtain cellulose membranes for permeation.

TABLE I

Adequate Condition for Preparation of Cellulose Membranes from Mixtures of Cellulose, Dimethylsulfoxide, and Paraformaldehyde[a]

Cellulose (g)	PF (g) 2.5	5.0	7.5	10	15	20	30
0.3	...	△	△	△	△	△	—
0.5	△	△	△	△	△	△	△
1.0	△	△	○	○	○	—	—
1.5	I	○	○	○	●	—	—
2.0	I	○	○	○	●	—	—
2.5	I	○	○	○	●	—	—
3.0	I	◑	◑	○	●	●	—

[a]DMSO content is 80 g. ○, homogeneous transparent strong membrane; △, heterogeneous weak membrane; ◑, heterogeneous strong membrane; ●, membrane preparation is impossible because viscosity of casting mixture is very large: I, cellulose is insoluble.

Effect of Membrane Thickness

The relationship between the rate of pure water permeability and the membrane thickness is shown in Fig. 1. In all systems the pure water permeabilities decrease with an increase in membrane thickness. These decreases of pure water permeability beyond a membrane thickness of 30 μm are very small. Below 30 μm a remarkable decrease of the rate of pure water permeability with the membrane thickness occurs. This result is due to an increase of thickness of a symmetric membrane because the casting solution to prepare the membrane below 30 μm is smaller and DMSO evaporates completely. On the other hand, above 30 μm DMSO is not completely evaporated under the experimental condition because its amount is higher. Therefore, the resulting membranes may be asymmetric. The dense surface layer in the overall membrane thickness acts as permeation resistance. The rough layer only supports the dense surface layer. The corresponding variations of the rate of pure water permeability are attributed to the thickness of the dense surface layer.

Effect of Cellulose Concentration

The effect of cellulose concentration on the membrane characteristics is depicted in Fig. 2. The rate of pure water permeability and the permeation rates for aqueous solutions of PEG 200, 1000, and 6000 decrease with an increase of the cellulose content in the casting mixture. The rejection for

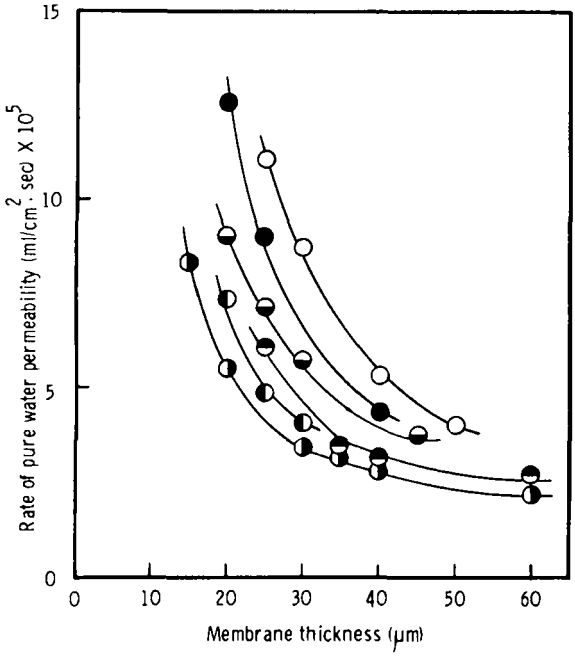

FIG. 1. Relation between pure water permeability and membrane thickness. Casting mixture composition: (○) Cellulose/DMSO/PF = 1/80/10 (g), (●) cellulose/DMSO/PF = 2/80/10 (g), (◓) cellulose/DMSO/PF = 3/80/10 (g), (◐) cellulose/DMSO/PF = 2/80/5 (g), (◑) cellulose/DMSO/PF = 2/80/7.5 (g), (◒) cellulose/DMSO/PF = 2/80/12.5 (g); preparation temperature of membrane: 110°C; operating conditions: 40°C, 4 kg/cm^2.

PEG 200 and 6000 are 0 and 100%, respectively, regardless of the cellulose content. Kleman et al. (*10*) and we (*5, 11*) have reported that the magnitude of the average pore radius decreases with an increase in concentration of cellulose acetate and poly(γ-methyl L-gultamate) in membranes of these polymers. The results in Fig. 2 suggest that the membranes prepared from higher cellulose concentrations are denser than the membranes with lower cellulose concentrations.

As can be seen from Fig. 2, the permeation rates for aqueous solutions of PEG 200, 1000, and 6000 are greater than the rate for pure water permeability. In general, it is well known (*12–16*) that water molecules form water "clusters" connected by hydrogen bonds. The size of a water cluster is governed by the temperature of the feed, the concentration and kind of the feed solute, and the kind of membrane materials. In the permeation of aqueous soluitons of PEG through cellulose membranes, the water is degraded in some degree because the PEG and cellulose molecules are

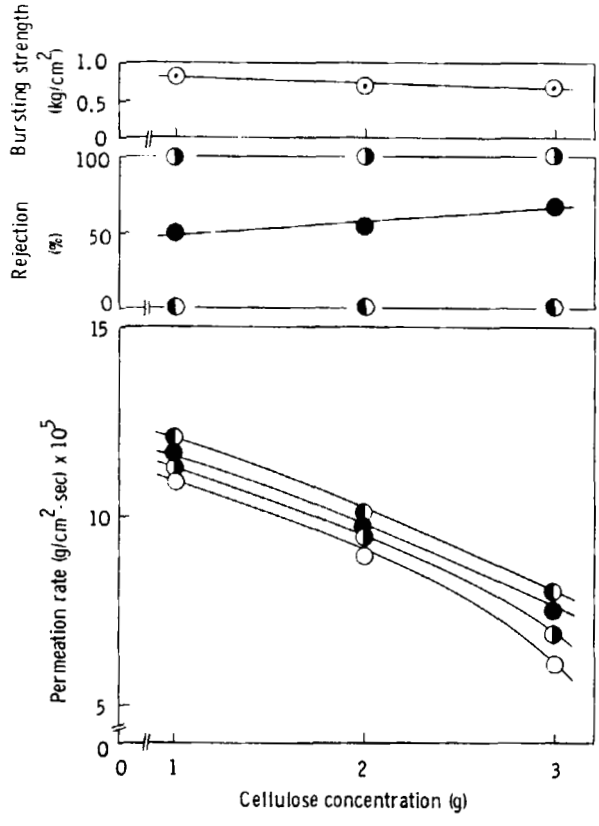

FIG. 2. Effect of cellulose concentration on membrane characteristics. Casting mixture composition: Cellulose/DMSO/PF = X/80/10 (g); preparation temperature of membrane: 110°C; membrane thickness: 20–25 μm; feed: (○) pure water, (◐) PEG 200, (●) PEG 1000, (◑) PEG 6000 1.0% aqueous; operating conditions: 40°C, 4 kg/cm^2.

hydrophilic. Furthermore, a PEG molecule brings about an activation of the movement of water molecules that attach the very weak layer on the membrane surface and in the membrane, promotes the permeation of attached water molecules, and consequently extends the apparent effective pore size in the membrane. The greater permeation rates for PEG aqueous solutions are caused by the above factors. We will report in detail on the above discussion for the rate of pure water permeability and the permeation rates of aqueous solutions of alcohols in a later paper.

Effect of Paraformaldehyde Concentration

The effect of added amounts of PF on the membrane characteristics is shown in Fig. 3. The permeation rates for pure water, aqueous solutions of PEG, and the bursting strengths of the resulting membranes increase with an increase in PF content up to 10 g. When the added amount of PF is more than 10 g, the rate of pure permeability decreases and the degree of increase in the permeation rate of PEG aqueous solutions decreases. The rejections of

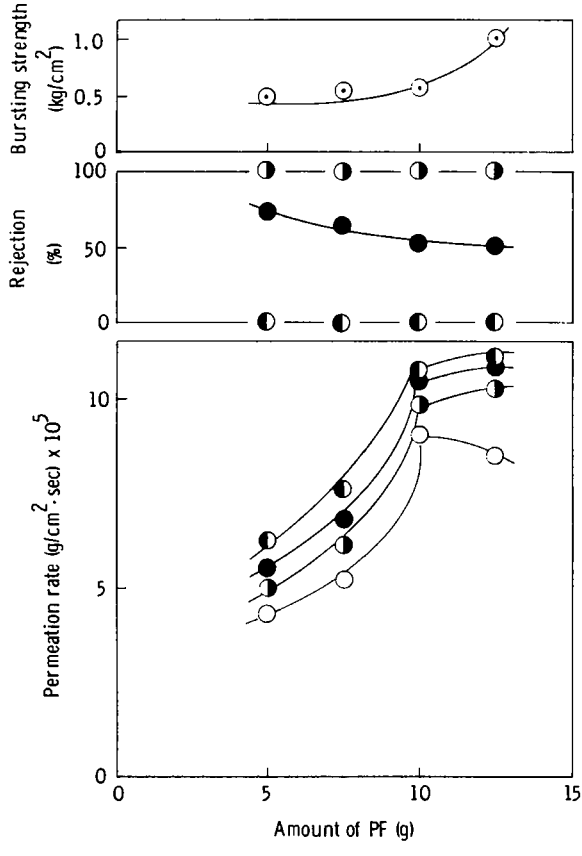

FIG. 3. Effect of added amount of paraformaldehyde on permeation characteristica and bursting strength. Casting mixture composition: Cellulose/DMSO/PF = 2/80/X (g); preparation temperature of membrane: 110°C; membrane thickness: 20–25 μm; feed: (○) pure water, (◐) PEG 200, (●) PEG 1000, (◑) PEG 6000 1.0% aqueous-solutions; (⊙): bursting strength; operating conditions: 40°C, 4 kg/cm^2.

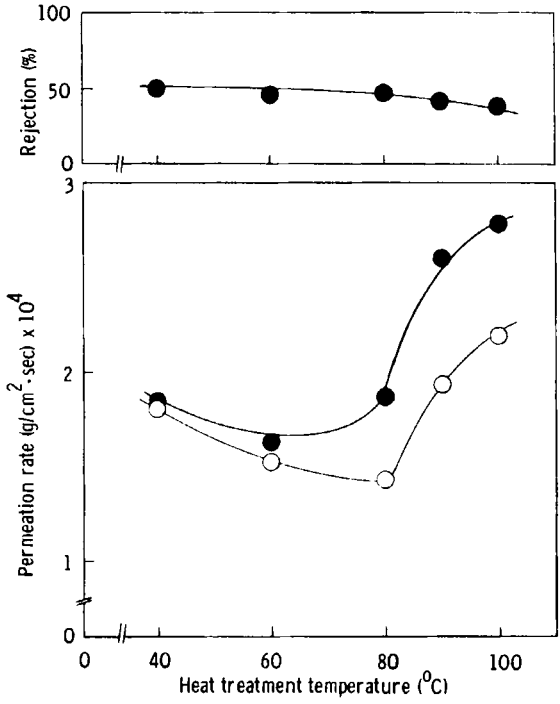

FIG. 4. Effect of heat treatment temperature on permeation characteristics. Casting mixture compositin: Cellulose/DMSO/PF = 2/80/10 (g); preparation temperature of membrane: 50°C; membrane thickness: 20–25 μm; feed: (○) pure water, (●) 1.0% PEG 1000 aqueous solution; operating conditions: 40°C, 4 kg/cm^2.

PEG 200 and 6000 are not changed and that for PEG 1000 decreses with the added amount of PF. It is well known that in the permeation through the polymer membranes the permeating species pass through amorphous region but not through the crystalline region. The increase of the amount of PF promotes the hydroxymethylation of cellulose molecules, the amorphousness in the resulting membranes increases, and consequently the permeation rate increases and the rejection of PEG 1000 decreases.

Effect of Heat Treatment

Figure 4 shows the effect of treatment in hot water on the permeation characteristics. The permeation rates for pure water and an aqueous solution of PEG 1000 decrease with increasing heat treatment temperature up to 80°C. Above 80°C these rates increase. The decrease of permeation rate up

to 80°C is dependent on a conversion from intramolecular hydrogen bonds into intermolecular hydrogen bonds in the amorphous region of the cellulose membrane. Since the molecular movements of cellulose and water molecules are more activated over 80°C, not only some intramolecular hydrogen bonds but some intermolecular hydrogen bonds of cellulose molecules may be severed. The activated water molecules enter into these severed parts, the fraction occupied by pure water in the membrane become larger, and consequently the permeation rates increase over 80°C. The fact that over 80°C the rejection of PEG 1000 decreases agrees with the above discussion.

Effect of Feed Concentration

Figure 5 shows the effect of feed concentration on the permeation characteristics, using aqueous solutions of ethyelenel glycol (EG) and PEG

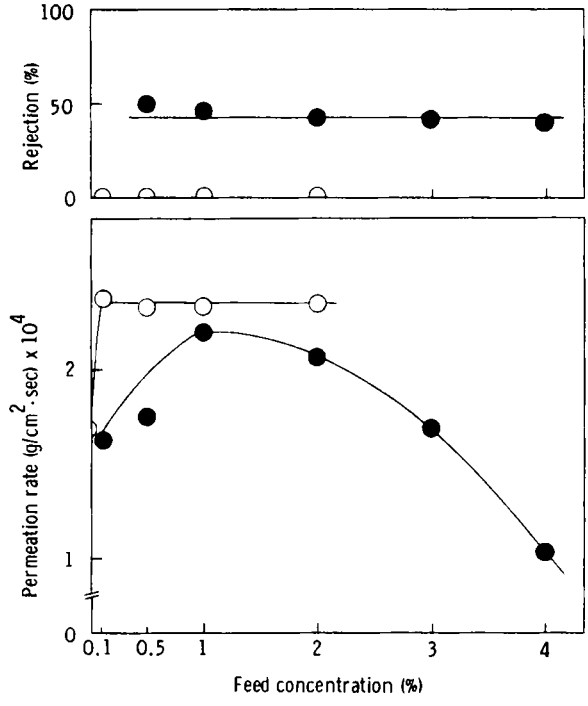

FIG. 5. Effect of feed concentration on permeation characteristics. Casting mixture composition: Cellulose/DMSO/PF = 2/80/10 (g); preparation temperature of membrane: 50°C; membrane thickness: 20 μm; feed: (○) EG, (●) PEG 1000 aqueous solution; operating conditions: 40°C, 4 kg/cm^2.

TABLE 2
Permeation Characteristics and Bursting Strength of Cellulose Membrane and Cuprophane Membrane

	Cuprophane membrane		Cellulose membrane[a]	
Membrane thickness (μm)	25		25	
Bursting strength (kg/cm^2)	0.4		1.0	
PWP (mL/cm^2·s)	1.2×10^{-4}		1.5×10^{-4}	
Feed solution[b]	PR (g/cm^2·s)	R (%)	PR (g/cm^2·s)	R (%)
PEG 200	1.0×10^{-4}	8.3	2.5×10^{-4}	9.1
PEG 1000	9.7×10^{-5}	62	1.8×10^{-4}	50
PEG 6000	1.0×10^{-4}	93	1.7×10^{-4}	100

[a]Cellulose/DMSO/PF = 2/80/10 (g), preparation temperature of membrane is 50°C.
[b]1.0% aqueous solutions; PWP, PR, and R are of pure water permeability, permeation rate, and rejection, respectively; operating conditions, 40°C, 4 kg/cm^2.

1000 as feed. The permeation rate for an aqueous solution of EG is constant regardless of the feed concentration. That for a aqueous solution of PEG 1000 has a maximum value at the feed concentration of 1.0%. The rejection of PEG 1000 is kept constant at 50%. A decrease of the permeation rate for a PEG 1000 aqueous solution depends mainly on an increase of the concentration polarization of PEG molecules onto the membrane surface with an increase of the feed concentration. The decrease is also related to increases of the viscosity and osmotic pressure of the feed solution. An increase of the permeation rate for a PEG 1000 aqueous solution up to 1.0% may be primarily attributed to an increase in the degree of deformation of the water cluster associated with it.

Comparison with Membrane Characteristics of Cuprophane

Table 2 summarizes the membrane characteristics of the cuprophane membrane which is used as a blood dialysis membrane for an artificial kidney and of the cellulose membrane prepared in this work. In spite of the fact that the rejections for PEG 200, 1000, and 6000 between the cellulose membrane and the cuprophane membrane are approximately equal, the permeation rates of these aqueous solutions through a cellulose membrane are always greater than those of cuprophane. In particular, it is worth noting that the bursting strength of a cellulose membrane is about twice that of a cuprophane membrane at the same membrane thickness. From these results, some of cellulose membranes prepared in this work may be expected to be

useful as artificial kidney membranes because of their permeabilities and bursting strengths.

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Received by editor June 1, 1981