

Plasma-Modified Nylon 4 Membrane for Dialysis

J. Y. LAI and C. C. CHOU, *Department of Chemical Engineering, Chung Yuan University, Chung Li, Taiwan, Republic of China*

Synopsis

The effects of plasma treatment conditions, such as supply power, treatment time, gases used in reactor, surface energy, water content, dialysis permeability, partition coefficient, diffusion coefficient, and free volume of Nylon 4 membranes, were studied. The solutes considered for dialysis system were NaCl, urea, and MgCl_2 . The permeabilities of NaCl and urea of membranes with plasma treated in argon at 80 W for 20 min are 5.57×10^{-5} and 5.89×10^{-5} cm^2/min , respectively. Much higher permeabilities of NaCl and urea obtained by oxygen plasma-treated membranes under 20 W and for 20 min are 30.74×10^{-5} and 17.66×10^{-5} cm^2/min , respectively, compared to that of untreated Nylon 4 membranes.

INTRODUCTION

Previous works on Nylon 4 membranes had been carried out by Lonsdale et al. and by Orofino (cited by Huang et al.^{1,2}), who found that Nylon 4 membranes behaved erratically in terms of their transport fluxes. Using the improved poly(pyrrolidone) synthesis and membrane preparation method, improved performance of Nylon 4 membranes was reported by Huang et al.^{1,2}

To improve the performance of Nylon 4 membranes, Lai et al.³ used ^{60}Co irradiation which induced hydrophilic vinyl monomers to be grafted onto Nylon 4 membranes for reverse osmosis desalination purposes. Jong et al.⁴ used a chemical method to graft different hydrophilic monomers onto Nylon 4 membranes for reverse osmosis, ultrafiltration, and electrodialysis.

Glow discharge (plasma deposition) has been used to increase surface energy, plasma polymerization, etching in membrane modification,⁵⁻⁷ and biomedical application.⁸

The purpose of this study is to improve the surface energy and water content, thereby increasing transport fluxes of Nylon 4 membranes by plasma modification for dialysis.

The effects of plasma treatment conditions, such as supply power, treatment time, gases used in reactor, surface energy, water content, dialysis permeability, partition coefficient, diffusion coefficient, and free volume of Nylon 4 membranes, were studied. The solutes considered for dialysis system were NaCl, urea, and MgCl_2 .

EXPERIMENTAL

Polymer Synthesis

Nylon 4 was synthesized by CO_2 -initiated polymerization of 2-pyrrolidone using potassium 2-pyrrolidonate as a catalyst.³ The molecular weights of

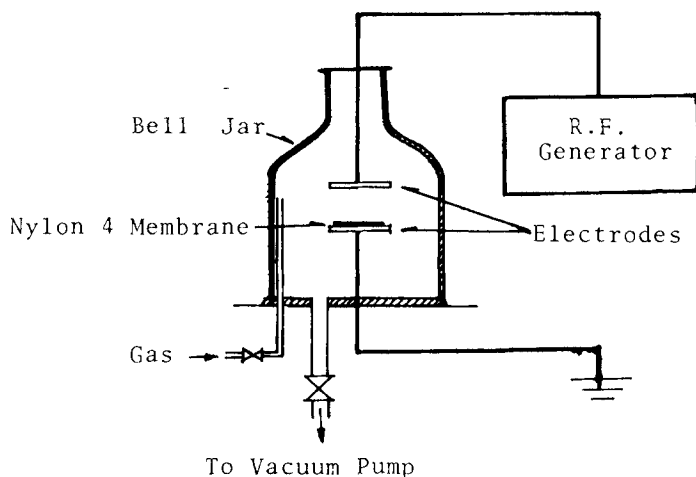


Fig. 1. Plasma reactor.

samples, measured by a Cannon-Fenske viscometer with *m*-cresol as a solvent at 25°C, were about 30,000–36,000.

Membrane Preparation

Dialysis membrane was prepared from a formic acid-casting solution of Nylon 4 added with *n*-PrOH as a swelling agent.^{2,3} The detailed procedure of the membrane preparation was according to our previous report.³ The casting condition for the membrane was heat treatment at 30°C for 40 min to evaporate solvent and provide suitable pore size of membranes. The membrane thickness was in the range of 20–40 μm.

Plasma Treatment

Bell jar-type plasma deposition system PD-2S (Samco Ltd., Japan), is shown in Figure 1. The membrane was plasma-treated at a pressure of 0.15 torr, a frequency of 13.56 MHz, and the range of supply power from 10–100 W for 1–30 min.

Water Content

Clean and dried membranes with known weights were immersed in distilled water at room temperature overnight to reach equilibrium swelling. The membranes were removed and quickly blotted with absorbent paper to remove surface liquid, and weighed quickly. The degree of water content was calculated by the following equation:

$$\text{Water content (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

where W_{wet} and W_{dry} represent the weights of wet and dry membranes, respectively.

Surface Energy

Contact angles of water, formamide, ethylene glycol, and tricresyl phosphate, on the membranes were measured with a Contact Angle Viewer Model D-1060 (Kayeness, Inc) at 25°C. The contact angle data were used to estimate the surface energy by Kaelble's method.⁹

Dialysis Permeability

A stainless cell consisting of two compartments (171 cm³ each) was used. A membrane was clamped between two compartments using suitably supporting and sealing devices. One of the compartments was filled with distilled water; the other with testing solution of NaCl, urea, or MgCl₂. The solution in the compartments were stirred during measuring their permeabilities and kept in water bath at 37.0 ± 0.5°C.

The permeability P (in cm² min⁻¹), under the assumption of neglecting liquid film resistance of both side of membrane, was calculated from¹⁰:

$$\ln \frac{C'' - C'}{C'' - C' - 2C(t)} = \frac{2PA}{\delta V(t)} t \quad (1)$$

where $V(t)$ is the volume of the solution at time t , A , the effective membrane area (24.28 cm²), δ , the membrane thickness, C'' and C' , the concentration of the concentrate and diluent compartments at initiation, respectively, $C(t)$, the concentration of diluent compartments at time t . Concentration of NaCl and MgCl₂ were determined by a Conductivity Meter Model SC-15 (Suntex). The urea permeate was added with urease to hydrolyze to NH₄⁺ and CO₃⁻² ions. Ion concentrations, NH₄⁺ and CO₃⁻², were also determined by the conductivity meter.¹¹

Density

Density of the plasma-treated membrane was measured at 25°C using a density gradient column filled with mixtures of varying solutions of carbon tetrachloride and *n*-hexane.

Hydration

The weighed membrane sample was immersed in the solution having the same concentration (C') as the solution in the diluent compartment. After equilibrium, the membrane sample was dried between two sheets of filter papers and weighed again. By extrapolation of the linear part of the curve to time zero, the weight of the swollen membrane sample at time zero was determined; and subsequently, the weight was converted into the volume of the swollen membrane sample by using the density of the plasma-treated membrane. Hydration of the membrane sample, H , was calculated according to the following equation:

$$H = \frac{\text{volume of the solution in swollen membrane}}{\text{volume of the swollen membrane}} \quad (2)$$

Partition Coefficient

The dried membrane samples were immersed and equilibrium was reached in the same solution concentration as concentrate solution compartment of the cell at $37.0 \pm 0.5^\circ\text{C}$. After removing the membrane sample, any extra surface solution was removed with filter paper. The membrane sample was then kept in distilled water with shaking for at least 2 h. The amount of solute extracted from the swollen membrane sample by the distilled water was determined by the method discussed previously. Partition coefficient K_2 was calculated by the following equation:

$$K_2 = \frac{\text{grams solute per } 1 \text{ cm}^3 \text{ swollen membrane}}{\text{grams solute per } 1 \text{ cm}^3 \text{ solution}} \quad (3)$$

Diffusion Coefficient

In general, the diffusion coefficient $D_{2,13}$ of the solute in a swollen membrane can be related to permeability $P_{2,13}$ in the following equation:

$$D_{2,13} = P_{2,13}/K_2 \quad (4)$$

where the subscripts 1, 2, 3 and 13 refer to water, solute, polymer, and water-swollen polymer, respectively.

RESULTS AND DISCUSSION

Membrane Resistance

The dialysis resistances are included for both sides of the liquid film resistances, which were affected by stirring of bulk solution, and diffusivity resistance of solid membrane. In order to understand which error might be caused by using Eq. (1) for determining dialysis permeability, the effect of stirring speed of dialysis compartments on the liquid film resistance was studied first. The plot $1/P$ versus $1/\text{rpm}$ of stirring was shown in Figure 2 where $1/P$ reaches the minimum value as rpm approaches to infinite; in other words, liquid film resistance approaches to zero. It indicates that the diffusion resistance and hence the dialysis permeability determined at 300 rpm used most often in the runs in this study would be about 11% below the theoretical value.

Surface Energy

As shown in Figure 3, water contact angle decreases from 73° to 30° , respectively under untreated circumstances and under 20 W power supply with 20 min plasma-treated time in oxygen for Nylon 4 membrane. The surface energy increases, mainly due to increasing polar term, with increase oxygen plasma treatment time. The surface energy of 20 min oxygen plasma-treated membrane is 61.2 dynes/cm and that of untreated membrane is 42.6 dynes/cm. Under the same conditions, using argon and nitrogen in plasma reactor, the contact angles are 42° and 46° and the surface energies, 54.8 and 54.2 dynes/cm, respectively.

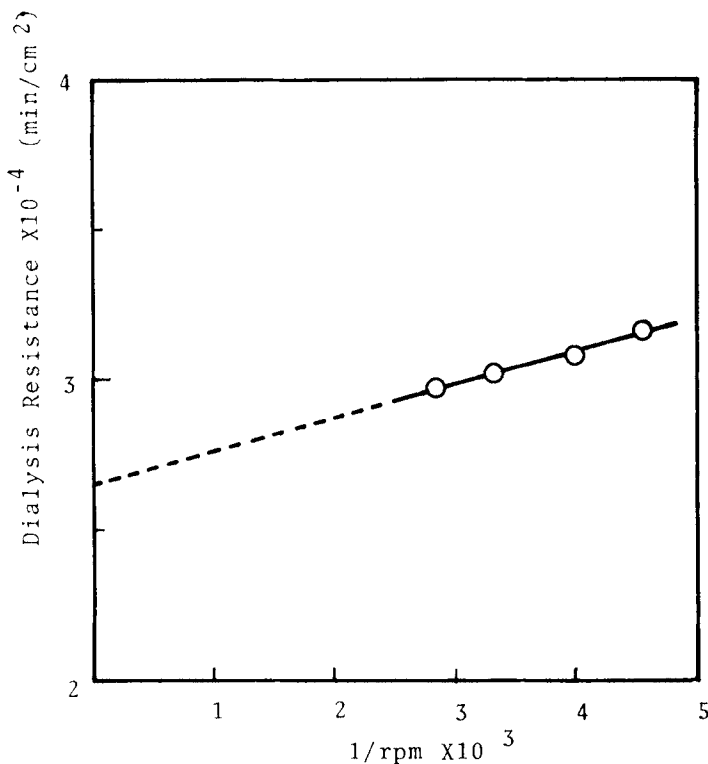


Fig. 2. Effect of stirring speed on dialysis resistance.

Water Content and Hydration

Figure 4 shows that both water content and hydration increase with increasing O₂ plasma treatment time in the considerable range of 0–20 min at 20 W. Water content and the hydration are increased for 20 min plasma treatment time to 55% and 0.175, respectively, compared to those of untreated membrane (42% and 0.104, respectively). It confirms the previously mentioned fact of increasing surface energy with increasing O₂ plasma treatment time. In our previous report,³ the water content of sodium styrene sulfonate X-ray-grafted Nylon 4 membrane with hydrophilic polymer chain increased more than did the plasma-treated Nylon 4 membrane with introduced hydrophilic functional group.

The high water content or hydration means that the macromolecular segments could be separated further in the presence of water. The water permeated from the membrane would be influenced by the water content or hydration of membrane. This result might be applied on modification of Nylon 4 membrane for ultrafiltration and reverse osmosis processes.

Effect of Plasma Gases

Figures 5 and 6 show that the dialysis permeabilities of the plasma-treated Nylon 4 membranes are increased with increasing supply power for 20 min of plasma treatment in oxygen, nitrogen, or argon gas. The permeabilities are

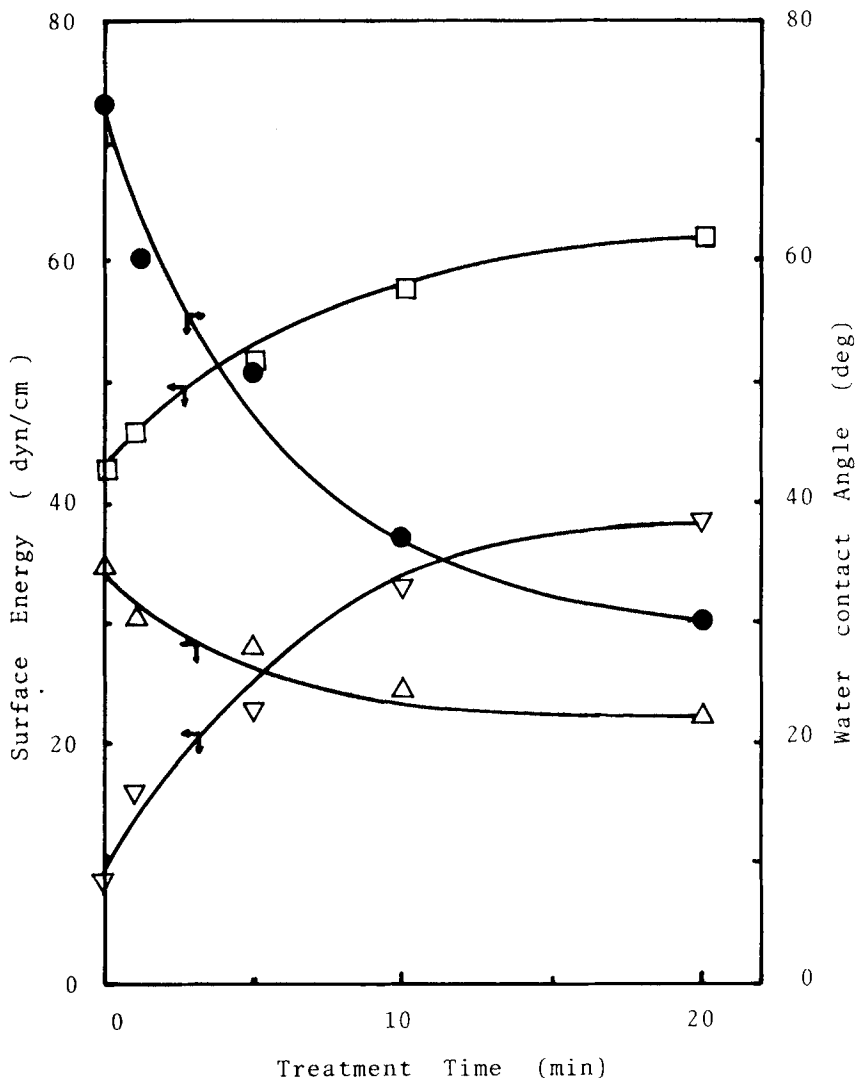


Fig. 3. Effect of O_2 plasma treatment time on surface energy and water contact angle. Surface energy: □, total; ▽, polar; △, dispersion; ●, water contact angle.

significantly increased starting at 20 W for plasma treating in oxygen, while it is appreciably and slightly increased at 80 W for treating in argon and nitrogen, respectively. Among the three gases considered in this study, the required activation energy for oxygen to form active radical is the lowest, while that of nitrogen is the highest. The existence of plasma-active radical of oxygen would cause the oxidation and etching effects with polymer chain of Nylon 4.¹² With higher energy supply, argon would be excited and transfer the energy to the polymer chain which could be activated with oxygen from air causing less oxidation and etching effect than plasma treatment in oxygen. There is no oxidation between active radical nitrogen and polymer chain of Nylon 4.⁵ This might explain the observed results.

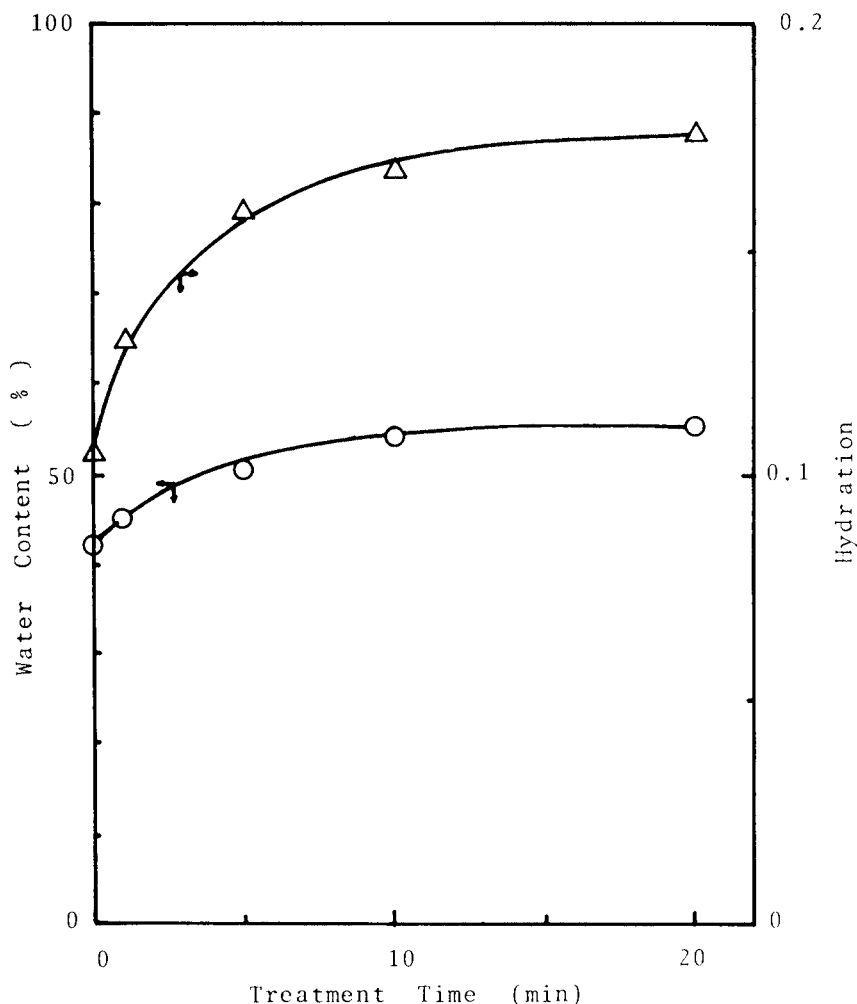


Fig. 4. Effect of O_2 plasma treatment time on water content (○) and hydration (Δ).

Effect of Treatment Time

The supply power of plasma reactor was fixed at 20 W, which was considered suitable from the results of the previous section for the oxygen plasma treatment time study. As shown in Figures 7 and 8, the solute permeabilities and diffusion coefficients are increased as the plasma treatment time increases up to 5 min. This could be caused by the increases of hydrophilicity, surface energy due to increasing of polar hydrophilic groups, such as ketone, hydroxyl, and ether.¹²

The solute permeabilities and diffusion coefficients are significantly increased with plasma treatment time longer than 5 min. The etching effect plays an important role in the increased solute permeabilities for longer plasma treatment times. This is verified by SEM study as shown in Figure 9. Partition coefficient is related to properties and particle size of solute, pore size of membrane, and interaction between solute and membrane. The affini-

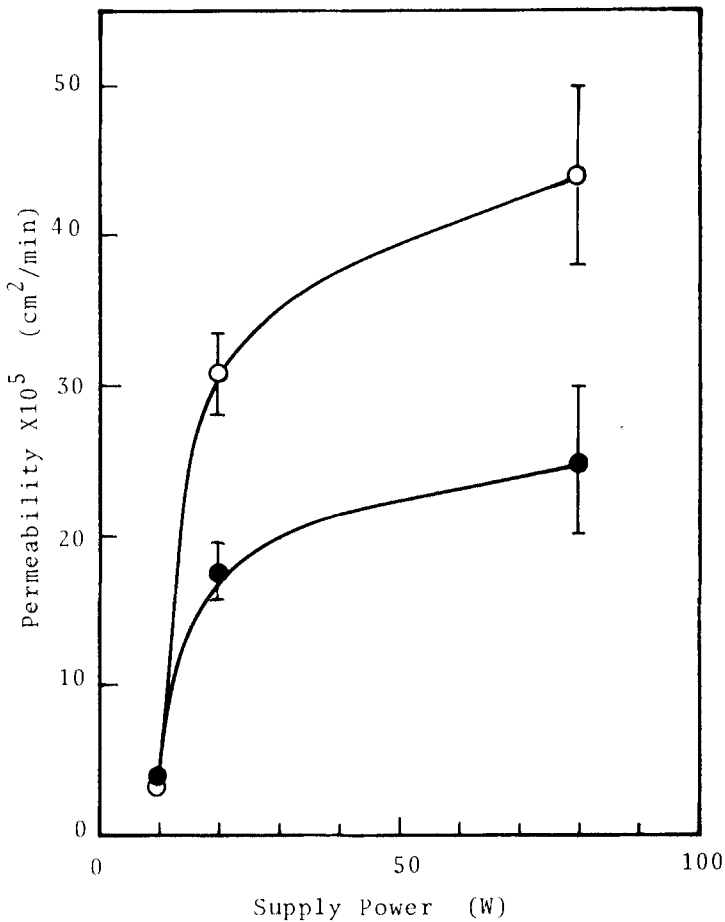


Fig. 5. Effect of supply power on permeability for plasma treatment in O₂. Solute: O, NaCl; ●, urea.

ties between Nylon 4 membrane and considered solutes are in the order of urea > NaCl > MgCl₂. Urea which has same amide group as Nylon 4, possesses stronger interaction with Nylon 4 and hence higher partition coefficient. As shown in Figure 10, the partition coefficients are decreased as oxygen plasma treatment time increases. This could be explained by the fact that the surface energy, hydration, and water content of plasma-treated membrane are increased with increasing polar chemical group while the solutes in the membrane are not proportionally increased.

Free Volume of Membrane

The diffusional transport of solute in aqueous solution through water-swollen membranes based on the concept of the free volume theory has been reported by Yasuda et al.¹³⁻¹⁶ The permeability $P_{2,13}$ of solute through

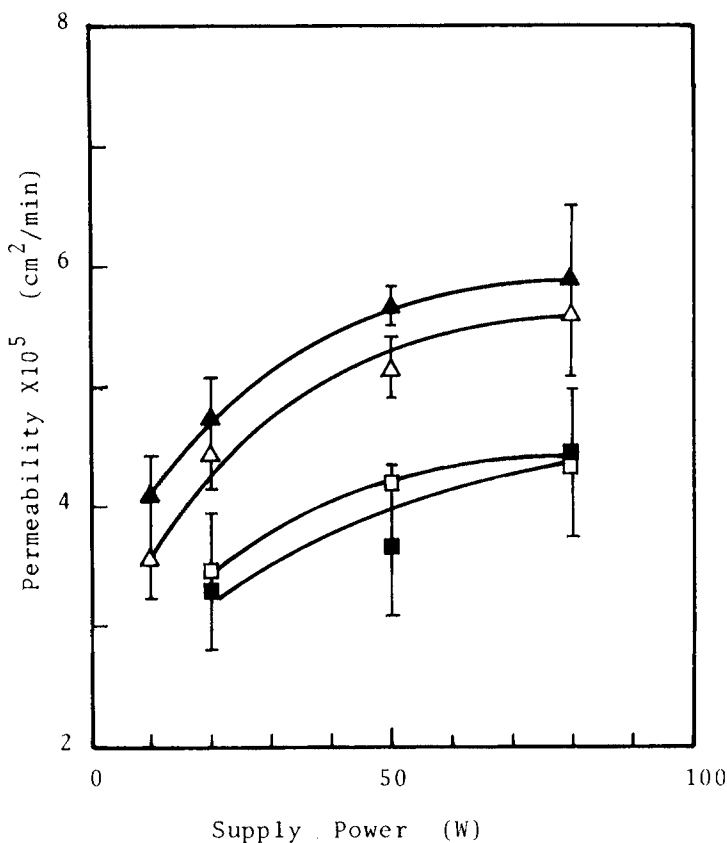


Fig. 6. Effect of supply power on permeability for plasma treatment in Ar and N₂. Gas: Δ , Ar; \square , N₂. Solute: open keys, NaCl; closed keys, urea.

homogeneously swollen membrane is expressed in the following equation:

$$P_{2,13}/D_{2,1} = K_2\varphi(q_2)\exp[-B(q_2/V_{f,1})(1/H - 1)] \quad (5)$$

$$\text{Log}(P_{2,13}) - \text{Log}[D_{2,1}K_2\varphi(q_2)] = -B(q_2/V_{f,1})(1/H - 1) \quad (6)$$

where $D_{2,1}$ is the diffusion coefficient of the solute in pure water, K_2 is the partition coefficient, $\varphi(q_2)$ describes the sieve mechanism by which small molecules are permitted to diffuse and larger molecules are rejected because the macromolecular network has no hole of appropriated size, $V_{f,1}$ is the free volume of pure water, q_2 is the cross-sectional area of the diffusing molecule, and B is a proportionality factor. The parameter of $B(q_2/V_{f,1})$ was used instead of $V_{f,1}$ to discuss the free volume of membrane.

As shown in Figure 11, $\log P_{2,13}$ decreases sharply with rising $(1/H - 1)$ value up to 5.33 and then decreases slightly with increasing $(1/H - 1)$, for NaCl, MgCl₂, and urea solutes. $B(q_2/V_{f,1})$ value, slopes after $(1/H - 1)$ value of 5.33, of urea, NaCl, and MgCl₂ are 0.026, 0.045, and 0.053, respectively.

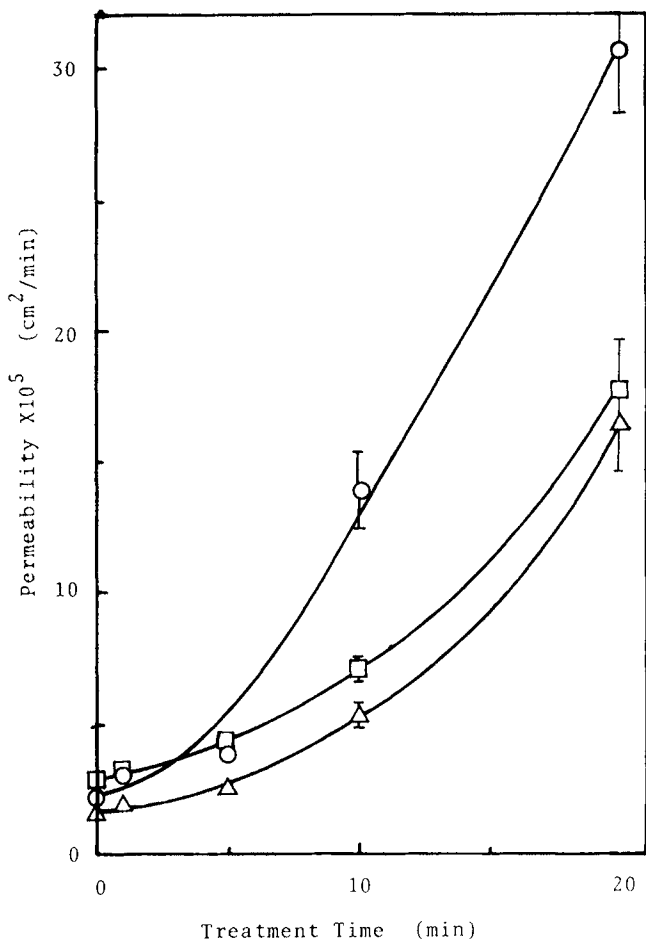


Fig. 7. Effect of O₂ plasma treatment time on permeability. Solute: O, NaCl; □, urea; Δ, MgCl₂.

This result indicates that the free volume concept of solute permeability through homogeneous swollen membrane is suitable to explain the observed solute permeabilities in the order of urea > NaCl > MgCl₂. For $(1/H - 1)$ value less than 5.33, it represents the data of the more porous membranes with longer time of plasma treatment in oxygen. Use of the above-mentioned concept in these porous membranes will give inadequate values.

COMPARISON TO THE RESULTS OF PREVIOUS WORKERS

Table I shows that the solute permeabilities of Nylon 4 membrane are much lower than that of commercialized Gambro membrane and X-ray irradiation-grafted acrylamide (AM) onto cellulose acetate and cellophane membranes. Membranes with oxygen plasma treatment for 5 min at 20 W or nitrogen plasma treatment for 20 min at 80 W possess about the same solute permeabilities as Gambro membrane. Permeabilities of NaCl and urea of membranes with plasma treated in argon at 80 W for 20 min are 5.57×10^{-5} and

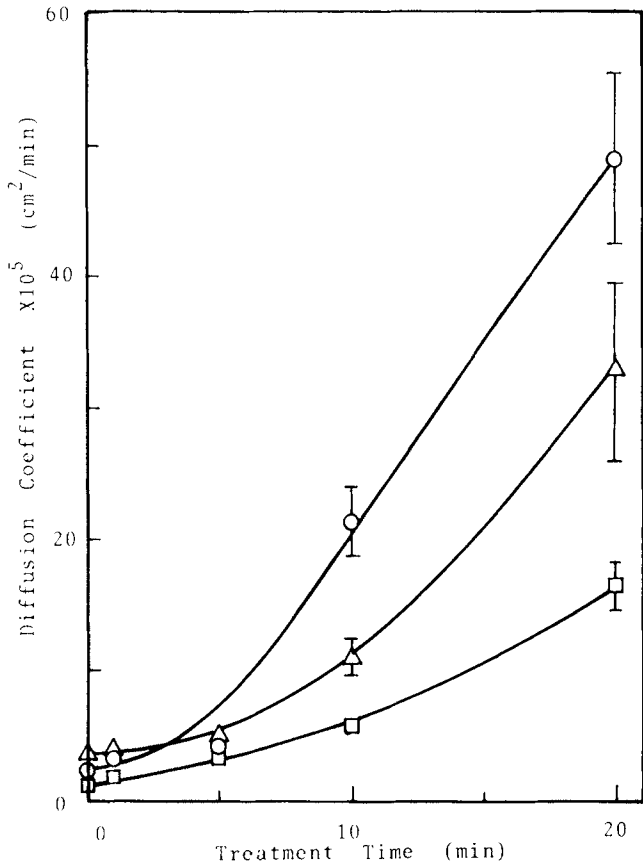
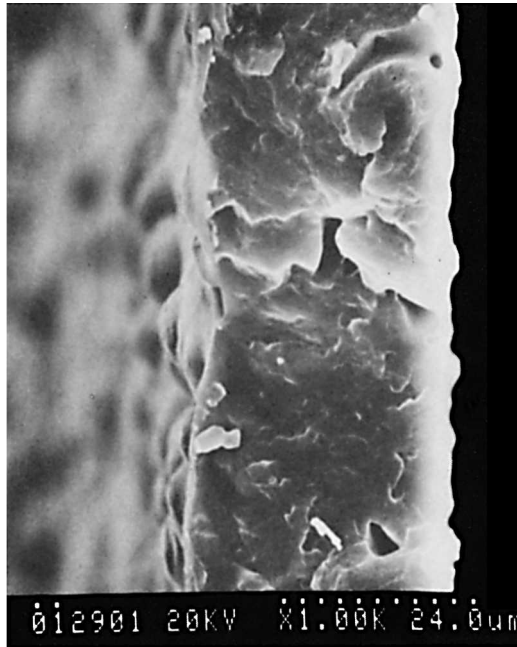
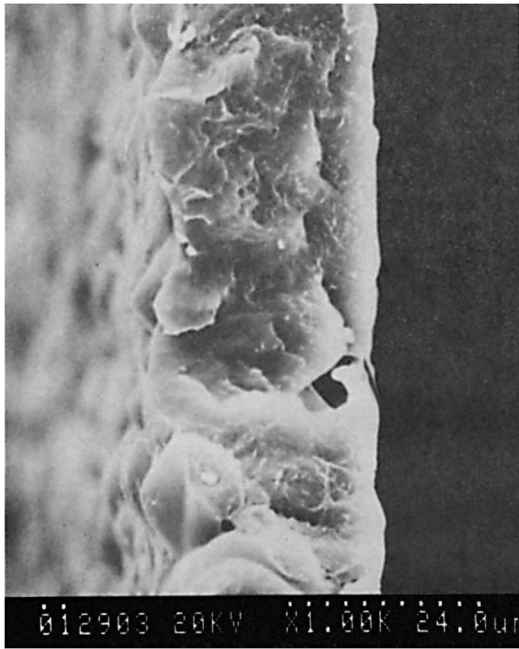


Fig. 8. Effect of O₂ plasma treatment time on diffusion coefficient. Solute: O, NaCl; □, urea; Δ, MgCl₂.

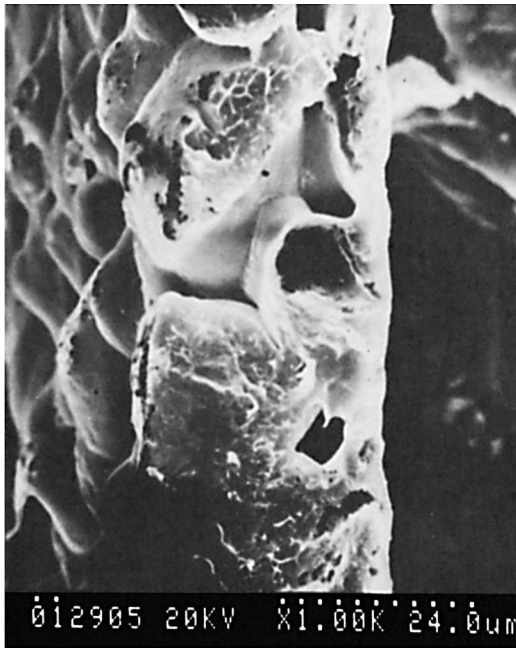


(a)

Fig. 9. Scanning electron micrographs of fractured face for plasma treated membranes: (a) untreated, (b) O₂ plasma 20 W-5 min, (c) O₂ plasma 20 W-20 min, (d) Ar plasma 20 W-20 min, (e) N₂ plasma 20 W-20 min.

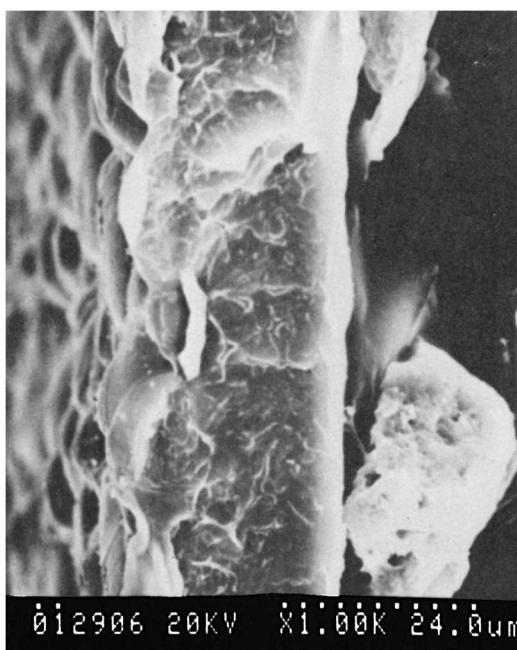


(b)

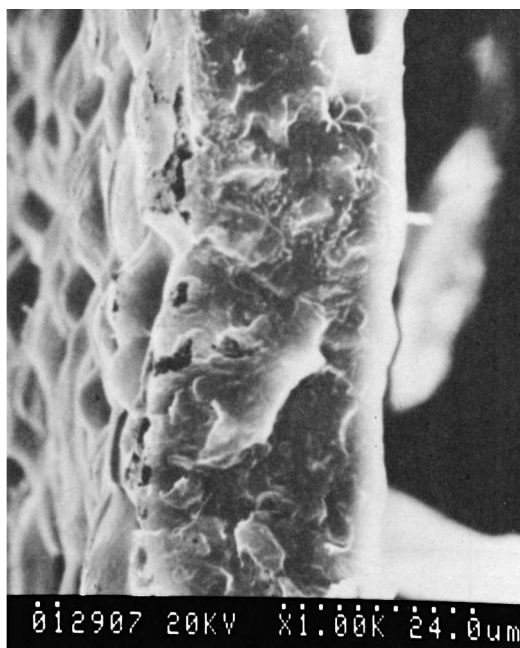


(c)

Fig. 9. (Continued from the previous page.)



(d)



(e)

Fig. 9. (Continued from the previous page.)

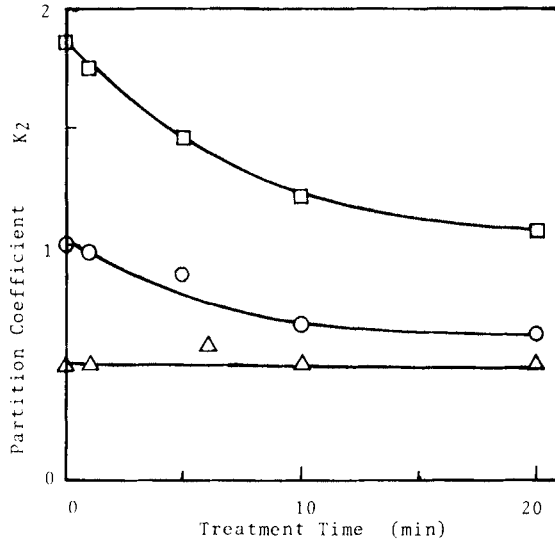


Fig. 10. Effect of O₂ plasma treatment time on partition coefficient. Solute: ○, NaCl; □, urea; △, MgCl₂.

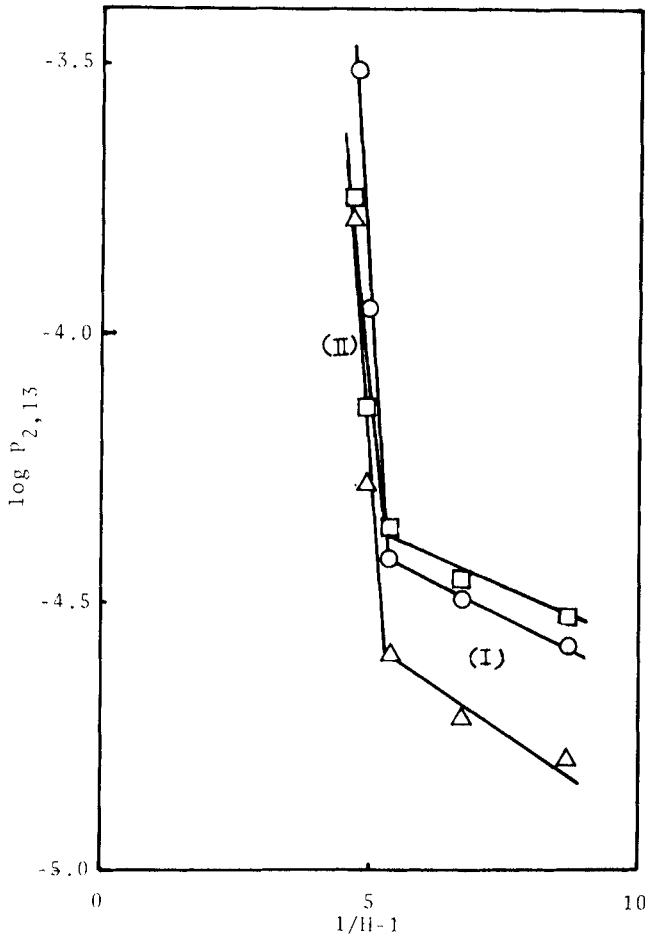


Fig. 11. Relationship between $\log P_{2,13}$ and $1/H - 1$ for NaCl (○), urea (□), and MgCl₂ (△).

TABLE I
Comparison of Previous Data with This Study

Membrane	Modified method	$P_{\text{NaCl}} \times 10^5$ (cm^2/min)	$P_{\text{urea}} \times 10^5$ (cm^2/min)	References
Gambro ^a (GLP11.5)	—	4.54	4.66	
PHEMA	—	1.50	4.20	17
Cellulose acetate	γ -ray acrylamide grafted	4.92	—	18
Cellophanes	γ -ray acrylamide grafted	—	7.43	10
Nylon-4	Untreated	2.72	2.98	This study
Nylon-4	Plasma treatment in O ₂ 20 W-5 min	3.82	4.37	"
Nylon-4	Plasma treatment in N ₂ 80 W-20 min	4.31	4.44	"
Nylon-4	Plasma treatment in Ar 80 W-20 min	5.57	5.89	"
Nylon-4	Plasma treatment in O ₂ 20 W-20 min	30.74	17.66	"

^aTest with Gambro membrane in our lab.

$5.89 \times 10^{-5} \text{ cm}^2/\text{min}$, respectively. Much higher permeabilities of NaCl and urea obtained by oxygen plasma-treated membranes under 20 W and 20 min are 30.74×10^{-5} and $17.66 \times 10^{-5} \text{ cm}^2/\text{min}$, respectively, compared to that of the above-mentioned membranes.

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