Pervaporation Membranes for Ethanol–Water Mixture Prepared by Plasma Polymerization. III. Perfluorocarbon Membranes

TOSHIO MASUOKA,* TAKASHI IWATSUBO, and KENSAKU MIZOGUCHI

Research Institute for Polymers and Textiles, 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan

SYNOPSIS

Pervaporation membranes for the ethanol–water mixture were prepared by plasma polymerization of tetrafluoroethylene, perfluoropropane, and perfluoropropylene onto porous substrates. The influence of the monomers on the elemental ratio (F/C) of the polymer depositions by X-ray photoelectron spectroscopy was rather small compared with that of the W/FM parameter (W = wattage for plasma excitation, FM = mass flow rate of a monomer). The optical emission spectroscopy indicated the similarity of gaseous species formed in the plasmas. The membranes were found ethanol-permselective, showing separation coefficients (α_{EtOH}) around 4–7 and a wide range of permeation rates (J), $10\text{--}10^{-2}$ kg/m^2 h, for the 4.8 wt % ethanol solution at 40°C. The α_{EtOH} of the membranes with thicker depositions could be correlated to the F/C ratios as a measure of membrane hydrophobicity. It was thought that, by making a plot α_{EtOH} against J values for the perfluorocarbon membranes, they could be classified into three groups on thickness of deposition. The ethanol-separation mechanisms for each group, which may contain four kinds of mass transfer schemes, i.e., distillation through larger pores, flow of sorption layer at the liquid–membrane interface, and diffusions through deposition or substrate, were also discussed.

INTRODUCTION

The unique characteristics of organic thin films prepared by the plasma polymerization technique have been investigated by many authors, and these films have been used as various industrial materials, i.e., as insulation films,[1] protection coating,[2] medical separation membranes,[3] and so forth.

In the field of separation membranes, the uniform solvent-resistant thin films are deposited normally on stable substrate membranes, forming composite membranes. They have already been applied to reverse osmosis (RO)[4,5] or gas separation.[6-8] Pervaporation (PV) is a relatively new application area,[9] in which the membrane is situated in between liquid and gaseous phases. The working environment of a membrane may be considered to be somewhere intermediate of RO and gas separation. Therefore, a composite type of separation membrane prepared by plasma polymerization may have a suitable structure for such a PV system, in which the importance of a substrate material as well as a permselective thin layer on top should be emphasized.

Although a variety of PV membranes other than plasma-polymerized membranes have been reported so far, ethanol-permselective membranes are found as rather exceptional cases, such as in silicone rubber[10] and fluoroalkyl acrylate-grafted polystyrene.[11] All these ethanol-permselective membranes seem to have hydrophobic structures.

In our previous papers,[12,13] by using a plasma polymerization of a mixed monomer system consisting of hexafluoroethane (HFE)–allylamine (AA), we could obtain thin layers with various degrees of hydrophobicity by changing the ratio of the monomer flow rates. The separation coefficient for ethanol increased with the hydrophobicity of the layers. By using perfluoropropane (PFP) monomer, a more

hydrophobic layer could be synthesized, exhibiting higher separation coefficients as predicted by the correlation.[14] However, the film growth was quite slow.

In this study, plasma polymerizations of various fluorocarbon monomers were investigated to search for conditions to prepare even more hydrophobic films at higher growth rates. Effects of monomer structure and the plasma reaction condition upon the produced polymer structure in conjunction with the PV performance for ethanol enrichment will also be discussed. For development of the practical PV membranes, plasma polymerization should expect to give an interesting model system to explore still ambiguous relationships between membrane structures and separation performance.

EXPERIMENTAL

Materials

Perfluoropropane (PFP) and perfluoropropylene (PFPP) were purchased from PCR Inc. and tetrafluoroethylene (TFE) was obtained from Takachiho Chemical Ind. Inc. These monomer gases were used for plasma polymerization without further purification.

As substrate membranes, we used two kinds of polysulfone (PS) filters with average pore sizes of 0.1 and 0.2 μm and thickness of about 100 μm, produced by Brunswick Technetics Co. These substrates had quite similar asymmetric structures, consisting of two layers, i.e., a thin dense layer (about 0.1 μm thick) on one side supported by a thick spongelike layer.[12,13] The plasma-polymerized films were deposited only on the side of the dense layer.

Membrane Preparation and Characterization

The plasma polymerization reactor used was basically the same type of the tubular reactor made of Pyrex glass as described in the previous paper,[13] but the size was larger (360 mm long, 70 mm id) to treat larger substrates. A pair of ring-shaped outer electrodes (1 cm width of aluminum bands) was attached to the upstream side for excitation of plasmas by a power source, Nippon Kosyuha Model SKN-05P, at 13.56 MHz radio-frequency (RF).

The substrate was placed perpendicular to the gaseous flow at about 6 cm on the downstream side from the nearest electrode to obtain homogeneous deposition.[14] However, on the edge region of the substrate, somewhat heterogeneous deposition could be observed. Therefore, only the central part was used for various measurements. RF wattages and monomer flow rates selected were in the ranges of 30–100 W and 2–8 stp-cm^3/min (sccm), respectively. Deposition rate (film-growth rate) was measured by the weight method in which the density of the thin film deposited on aluminum foil substrates was assumed to be 1.0 g/cm^3. During plasma polymerization, optical emission spectroscopy (OES) was performed to monitor plasma conditions by using a JASCO CT-10 monochromator with an optical fiber assembly at a scan rate 60 nm/min.

The plasma-polymerized membranes were characterized by Shimadzu ESCA Model 750, an X-ray photoelectron spectrometer (XPS) with a MgKα X-ray source.

Measurement of Pervaporation Performance

The pervaporation cell used[14,15] had a 200 cm^3 glass reservoir for the feed solution, and the membrane to be examined was set on a porous stainless-steel support disk with a Viton rubber gasket, then evacuated from the other side of the disk. The pressure drop over the membrane was always 1 atm. During the measurement, the whole cell was dipped into a temperature-regulated bath kept at 40°C. The feed concentration was a 4.8 wt % ethanol aqueous solution. Permeated vapor was condensed in a small liquid-nitrogen-cooled trap (capacity = ca. 50 mL) to be weighed and analyzed by gas chromatography. In the vacuum line, two of the same traps with O-ring joints were connected parallel, each having Teflon stopcocks for inlet and outlet tubes. The traps were used alternatively so as to sample the permeate without disturbing evacuation. The separation coefficient (α_{EtOH}) was calculated by the equation

$$\alpha_{EtOH} = (X_{EtOH}/X_{Water})_{Permeate}/(X_{EtOH}/X_{Water})_{Feed}$$

where X is a weight percentage of a liquid component shown by the subscript letters. The permeation rate (kg/m^2 h) was calculated from the weight of the trapped permeate, effective diffusion area of a membrane (19.6 cm^3), and permeate-sampling period.

RESULTS AND DISCUSSION

Reaction Behavior of Perfluorocarbons

In this study, three kinds of perfluorocarbon monomers, TFE, PFPP, and PFP, were used to evaluate

the effect of monomer structures upon plasma polymerization behavior and the deposited polymer structures. In the previous study on the PV membranes by HFE–AA plasma polymerization,[13] we used the elemental ratios, F/C, of the membranes obtained by XPS as a tentative measure of hydrophobicity. We found positive correlation between the membrane hydrophobicity and α_{EtOH} values. However, even for the most hydrophobic membranes prepared in the system, the F/C values did not exceed 1.2 because nitrogen-containing polar groups, such as nitril or amino groups, coming from AA were always incorporated into the polymers. Therefore, these groups were not useful to improve membrane performance more.

In Figure 1, F/C values of polymer depositions estimated by XPS are correlated with the W/FM parameter, where W and FM are RF wattage and mass flow rate of a monomer, respectively. By using the W/FM parameter, the balance between two competitive processes taking place in a plasma, i.e., decomposition and polymerization, can be compared.[16-18] It is clearly seen that the F/C ratio decreases with the W/FM parameter, even though the F/C ratio is distributed in a relatively narrow range from 1.4 to 1.6 at a higher level, in contrast to those of the HFE–AA system in a range of 0.0–1.2.[13]

In Figure 2, the $\Sigma[-CF_3 + -CF_2-]\%$ value, i.e., the summation of area percentages of $-CF_3$ and

Figure 2 Dependence of $\Sigma[-CF_3 + -CF_2-]\%$ of fluorocarbon membranes from deconvolution analysis of C_{1s} peaks in XPS (see Fig. 1 for symbols).

$-CF_2-$ component peaks computed by deconvolution of the total C_{1s} peak of XPS is also plotted against the W/FM values. For a PFP–argon system, the $\Sigma[-CF_3 + -CF_2-]\%$ value was considered to be a more sensitive measure of a membrane's hydrophobicity compared with the simple F/C ratio.[14] However, as shown in Figure 2, the summation values did not always reflect the change of the F/C ratio, probably because the data from the three different perfluorocarbon systems were plotted together. It is, however, concluded that the films prepared here may be more hydrophobic than those from the HFE–AA system, as far as F/C values are concerned.

It should be also noted that W/FM dependence of the membrane hydrophobicity seems to be described by almost one common curve, as seen in Figures 1 and 2, especially at higher W/FM conditions. In other words, a similar structure of deposition can be obtained, regardless of perfluorocarbons polymerized, if a proper reaction condition is selected.

Under conditions studied, the deposition rates of the fluorocarbon polymers were found to be at several tens Å/min, at least one order of magnitude slower than that of a typical HFE–AA system in our previous work. Among the fluorocarbon monomers, the deposition rate of PFP polymer film was the slowest, at about one-half that of the other. That may be explained by the lack of polymerizable structures in the monomer molecule such as a double bond.[16] Despite sacrificing the deposition rate, for the purpose of membrane development, it was in-
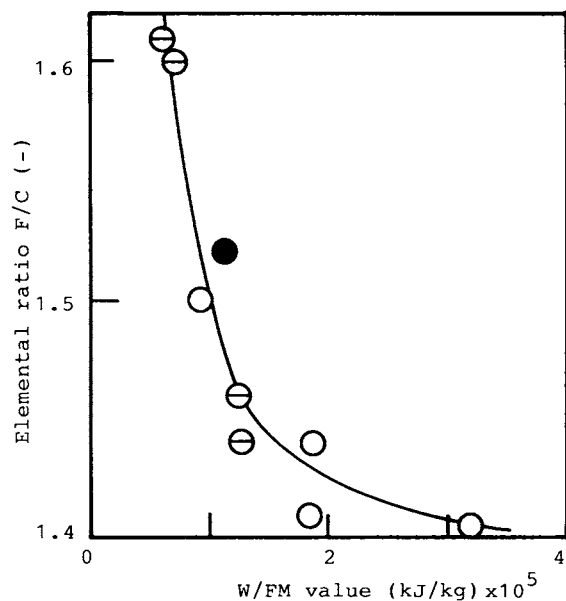

Figure 1 Plasma reaction parameter (W/FM) dependence of elemental ratio (F/C) of plasma-polymerized membranes measured by XPS: (●) PFP; (○) TFE; (⊖) PFPP.
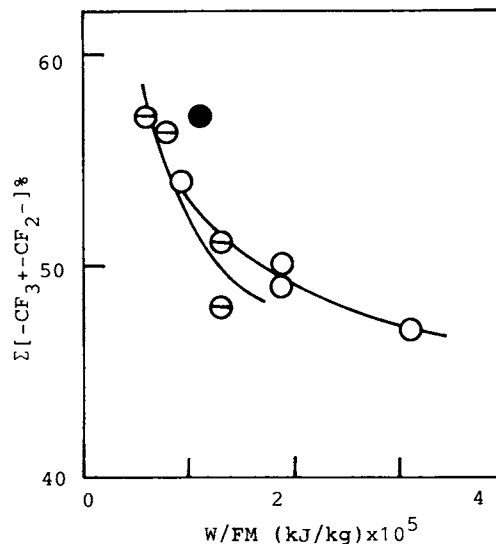
teresting to determine if the α_{EtOH} value could be really improved.

Optical Emission Spectra (OES) from Perfluorocarbon Plasmas

To characterize plasma states, OES has been widely used, although it may be difficult to assign most of the emission lines observed. In the systems investigated, emission spectra were measured at the same position as were substrates plasma-treated in the downstream side of RF electrodes. The OES from TFE and PFP plasmas are illustrated in Figure 3 and show the characteristic features of perfluorocarbon plasmas.[19] They contained intense emission lines from silicon fluorides (SiF· at 437 nm, and SiF$_2$· at 390 and 401 nm), which could be attributed to the etching products of the reactor glass wall in a plasma excitation region,[17,18] in addition to the relatively weak lines of fluorocarbon species (CF· and CF$_2$· in a region, 300–400 nm) evidently formed by monomer decomposition.

The silicon fluoride lines were observed to be weakened with polymerization time, probably due to the growth of deposition on the reactor wall, which reduced the glass etching. Finally, the lines only from fluorocarbon species persisted. The OES behaviors suggested the similarity of active species generated in the plasmas. That may be the reason why the relationships between the polymer structures (F/C ratio) and reaction conditions (W/FM) for the monomers studied here were almost the same,

namely, the polymer structures were not affected much by the monomer, but more by the reaction conditions.

Separation Performance of Plasma-Polymerized Membranes

W/FM dependence of α_{EtOH}

In this section, we used PS substrate with an average pore size of 0.1 μm, and polymerization time was 2 h, which might be long enough to deposit thick plasma polymer films for stopping the pores on the substrate completely. Therefore, it may be considered that the membrane performance discussed here is about the permeation through polymer deposition layers, not about open pores of the membranes.

Figure 4 shows the W/FM dependence of α_{EtOH} values for the plasma-polymerized perfluorocarbon membranes. Since F/C elemental ratios decreased with the increase of W/FM parameter, as shown in Figure 1, the α_{EtOH} increased with the F/C ratio, i.e., with the hydrophobicity of deposited films, and even more than that expected from the previous studies on the HFE–AA membranes.

Probably, an extreme case of the most hydrophobic membrane could be a polytetrafluoroethylene (PTFE) membrane. For a PTFE membrane, the F/C value should be almost 2. If a homogeneous thin film of PTFE were to be obtained and the correlation between the F/C and the α_{EtOH} is still valid, the membrane might exhibit much higher separation capability.
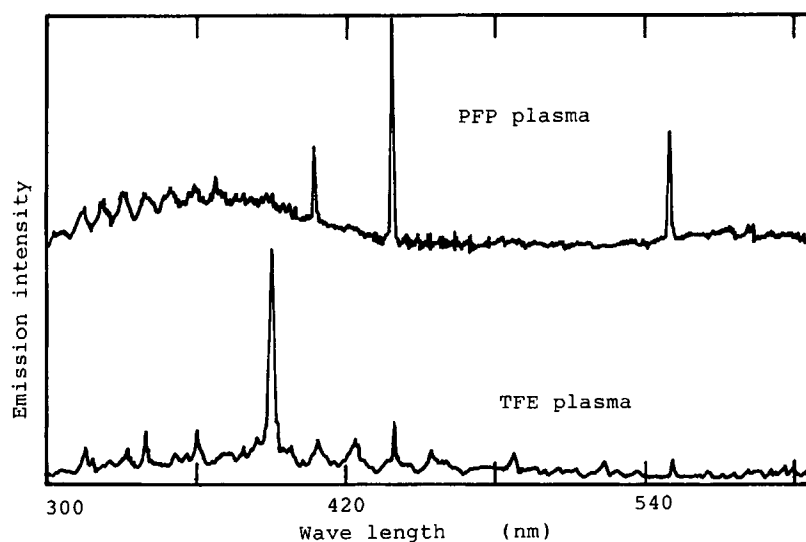

Figure 3 Emission spectra of fluorocarbon plasmas: PFP plasma, 50 W, 3.2 sccm; TFE plasma 50 W, 3.4 sccm.
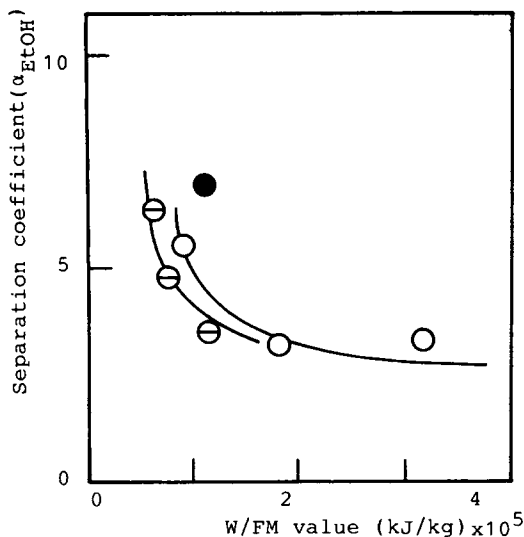
Figure 4 W/FM parameter dependence of ethanol separation coefficient, α_{EtOH} for 4.8 wt % solution at 40°C (see Fig. 1 for symbols).

Effect of Plasma Treatment Time

Before this study, we assumed that the deposition layer should have sufficient thickness; otherwise, the membrane separation might not occur due to the leakage of the feed solution. Thus, in the previous section, we discussed the membranes with sufficient thickness of deposition to cover pores on the substrate.

However, as shown in Figure 5, we discovered that the membrane PFP–plasma treated for a shorter time exhibited fairly good separation coefficients from 4 to 5 and higher permeation rates, about 10 kg/m² h.

In this section, the PS substrates had a larger average pore size, 0.2 μm, than that of the previous section. The change of the membrane performance with plasma treatment time is clearly demonstrated under the circumstance of a slow deposition rate of PFP polymer in addition to the larger pore size of the PS substrate.

The situations at the cross section of such higher-permeation-rate membranes are schematically described as (a) in Figure 5, in which open pores may still be left. According to the precise definition,[15] such membranes should not be called PV membranes.

After PFP–plasma treatment for about 220 min, the permeation rate started to decline. At almost the same moment, α_{EtOH} took a maximum value, about 7, then decreased slightly with the permeation rate. At that moment, the deposition thickness was found almost equal to 0.2 μm, the average pore size

of the substrate. The situation probably taking place on the substrate is shown schematically as (b) in Figure 5 in a cross-sectional view. After the polymer deposition grows sufficiently to block the substrate pores, situation (c) may occur. Scanning electron microscopy revealed that such a deposition process could really proceed on the substrate surface.[13,14]

Relationship between J and α_{EtOH}

In Figure 6, the α_{EtOH} value of the membranes prepared on the 0.2 μm pore-size substrates from perfluorocarbons under various conditions is plotted against the permeation rate. It can be seen from this plot that the membranes can generally be classified into three categories, i.e., the membranes with

1. the lowest permeation rates and α_{EtOH} values,
2. the higher permeation rates and α_{EtOH}, and
3. the medium permeation rates and highest α_{EtOH}.

These categories may generally correspond to the three situations, (a), (b), and (c), discussed in the above section. In this context, the structure–performance relationship of plasma-polymerized membranes should be discussed separately for each category of membranes, even though already-mentioned data may suggest that the membrane hydrophobicity may improve separation capability in any case.
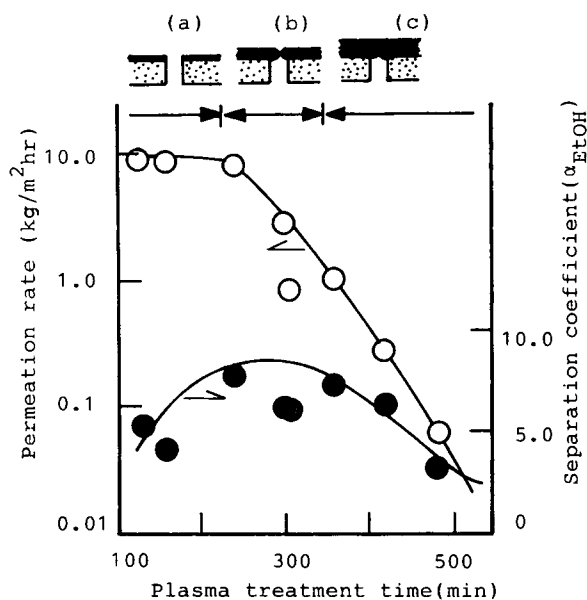

Figure 5 Dependence of membrane performance upon plasma polymerization time, i.e., membrane thickness: PFP flow rate = 3.2 sccm, wattage = 50 W.
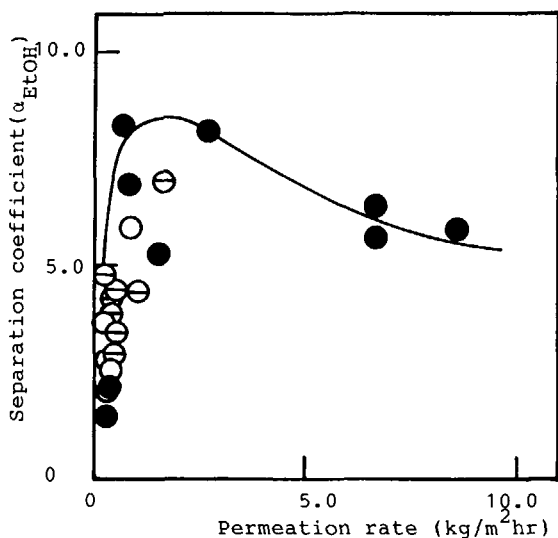
Figure 6 Relationship between separation coefficient and permeation rate of fluorocarbon membranes plasma-polymerized for 4.8 wt % solution at 40°C (see Fig. 1 for symbols).

All the situations may not arise separately, but could appear simultaneously on the same membrane, because, precisely speaking, any kind of porous substrates must have pore-size distributions. The more realistic situation may be schematically described as Figure 7, where the total mass flux (J) can be divided into four kinds of mass transfer phenomena, i.e., distillation of bulk solution through pores (Jp), flow of a sorption layer through pores (Js), diffusions through the deposition layer developed on pores (Jm), or through deposition on nonporous parts of a substrate (Jms). This is expressed as $J = Jp + Js + Jm + Jms$.

The contribution change of each flux may be described as in Figure 8, intuitively. The abscissa may
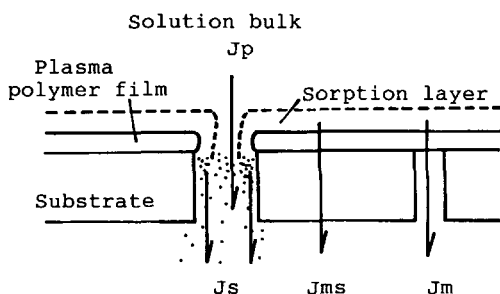

Figure 7 Illustration showing four ethanol separation schemes of a membrane with a highly hydrophobic layer on a porous substrate: Jp, distillation through uncapped pores; Js, flow of sorption layer through pores; Jm and Jms, diffusion through deposition on pore openings and on nonporous parts of a substrate, respectively.
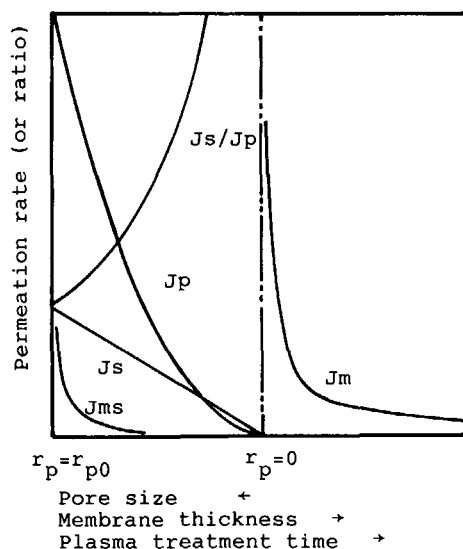

Figure 8 Schematic diagram showing contributive change of permeation flux by possible separation mechanisms upon plasma polymerization time (t) or thickness of deposition ie. the average pore size (r_p) remained at membranes surface ($r_p = r_{p0}$ at $t = 0$) (see Fig. 7 for notations).

denote plasma treatment time or deposition thickness or size of surviving pores. Since the quite hydrophobic layer was deposited from perfluorocarbon plasmas, it is likely to emerge as an ethanol-rich layer at the solution–membrane interface. The composition in the layer may be altered from that at normal solution–vapor equilibrium by the effect of the hydrophobic surface.

If the substrate pores are not fully stopped by hydrophobic deposition and if the pores, the sizes of which are in an order of a sorption layer thickness, are still existing, the flux Js may occupy a substantial portion in a total flux J. In this case, an α_{EtOH} value may be improved and, at same time, a higher permeation rate should be still retained. This kind of membrane must belong to group 3.

For the membranes with thicker deposition, the effects of preferential sorption, probably into the deposition, may be partially revoked due to the larger molecular size of ethanol than that of water, although the sorption at the interface is still advantageous to ethanol separation. Such membranes should have a lower permeation rate and α_{EtOH} value, i.e., they belong to category 1.

CONCLUSIONS

We investigated plasma polymerization of perfluorocarbons to prepare ethanol-separation membranes.

The F/C ratio and the total carbon percentage in the hydrophobic groups ($-CF_3$ and $-CF_2-$) of the produced membranes were greatly affected by plasma conditions designated by the W/FM parameter rather than by monomer structures. The smaller influence of monomer may be explained by the similarity of the gaseous species, as indicated by the OES.

The α_{EtOH} value for the 4.8 wt % ethanol solution at 40°C was found to increase with the hydrophobicity for membranes with thicker deposition of a plasma-polymerized layer.

With thickness of the deposition, the α_{EtOH} and the flux, J, were observed to be altered. At a specific thickness that was almost the same as a substrate pore size, the α_{EtOH} value was found to take a maximum. That might be explained by forming an ethanol-rich sorption layer at the membrane–solution interface.

The results suggested that hydrophobic deposition of an appropriate thickness onto substrates with high porosity and homogeneous pore-size distribution might be essential conditions for the practical membranes.

REFERENCES

1. Y. Segui, D. Montalan, and B. Moret, *Thin Solid Films,* **120,** 37–45 (1984).
2. H. P. Schreiber, M. R. Wertheimer, and A. M. Wrobel, *Thin Solid Films,* **72,** 487–493 (1980).
3. T. Masuoka, M. Ohnishi, and O. Hirasa, *Radiat. Phys. Chem.,* **33,** 421–427 (1989).
4. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.,* **17,** 201–222 (1973).
5. A. T. Bell, T. Wydeven, and C. C. Johnson, *J. Appl. Polym. Sci.,* **19,** 1911–1930 (1975).
6. A. F. Stancell and A. T. Spencer, *J. Appl. Polym. Sci.,* **16,** 1505–1514 (1972).
7. M. Kawakami, Y. Yamashita, M. Iwamoto, and S. Kagawa, *J. Membr. Sci.,* **19,** 249–258 (1984).
8. M. Yamamoto, J. Sakata, and M. Hirai, *J. Appl. Polym. Sci.,* **29,** 2981–2987 (1984).
9. S. Yamada and T. Hamaya, *Maku (Membrane),* **7,** 41–46 (1982).
10. S. Kimura and T. Nomura, *Maku (Membrane),* **8,** 177–183 (1983).
11. K. Ishihara and K. Matsui, *J. Appl. Polym. Sci.,* **34,** 437–440 (1987).
12. T. Masuoka, K. Mizoguchi, O. Hirasa, and A. Yamauchi, in *Proceedings of the 3rd International Conference on Pervaporation in Chemical Industry,* Bakish Materials Corp., Englewood, NJ, 1988, pp. 143–149.
13. T. Masuoka, T. Iwatsubo, S. Hongyou, and K. Mizoguchi, *Kagaku Kogaku Ronbunsyu,* **16,** 447–453 (1990).
14. T. Masuoka, T. Iwatsubo, and K. Mizoguchi, to appear.
15. S. Yamada, *Maku (Membrane),* **6,** 168–184 (1981).
16. H. Yasuda, *Plasma Polymerization,* Academic Press, Orlando, FL, 1984.
17. T. Masuoka and H. Yasuda, *J. Polym. Sci. Polym. Chem. Ed.,* **20,** 2633–2642 (1982).
18. T. Masuoka and H. Yasuda, *J. Polym. Sci. Polym. Chem. Ed.,* **19,** 2937–2946 (1981).
19. M. M. Millard and E. Kay, *J. Electrochem. Soc.,* **129,** 160–165 (1982).