Water–Ethanol Permseparation by Pervaporation through the Plasma Graft Copolymeric Membranes of Acrylic Acid and Acrylamide

TOSHIHIRO HIROTSU and SHIGERU NAKAJIMA,* *Research Institute for Polymers and Textiles, 1-1-4, Higashi, Tsukuba, Ibaraki 305, Japan*

Synopsis

Acrylic acid was copolymerized with acrylamide onto the porous polypropylene film which had been previously treated by glow discharge plasma, and the partially ionized membranes were prepared with treating in dilute sodium hydroxide aqueous solution. Using these membranes with different ratios of polyacrylate ion, water–ethanol permseparation was investigated. The membranes were water-permselective because of the hydrophilicity, and the permselectivity was increased by ionization generally for the feeds with ethanol concentration more than 50%. In the lower ethanol concentration range, the permselectivity was not so good because of the much higher permeation rate. When the permselectivity was evaluated by the products of separation factor (a) and Flux (Q), the copolymerized membranes with the acrylic acid mixing at 0.4 were superior to the ion-exchange membranes, although somewhat inferior to the ionized membranes of acrylic acid grafting which had been attempted previously. In the ionized membrane of the copolymer, the activation energy for permeation lied between 4.2 and 5.5 kcal/mol, and was much smaller than that of the neutral membranes before ionization; i.e., the decrease of flux was depressed even at the lower temperature.

INTRODUCTION

Much attention has been devoted to the membrane process for water–ethanol separation in recent years, and greater efforts have been made to develop the effective membranes. There are two types of the water–ethanol permselective membranes; i.e., water-permselective ones and ethanol-permselective ones. More hydrophilicity of the membranes is preferable for the permseparation of water, and therefore the incorporation of the ionic moieties in the membrane structure is effective to increase the permselectivity of water. For example, the ion-exchange membranes such as Nafion[1] and others[2] and the copolymeric membranes containing ionic groups[3] have been investigated for the water permseparation, and good results have been reported. The higher permselectivity of water through these membranes is possibly due to the higher hydrophilicity of the ionic groups to increase the affinity to water. In addition, the higher fluxes are obtained by the greater size of the permeation paths formed by the ionic repulsion.

---

*Present address: The Tokyo Metropolitan Textile Institute, 3-15-3, Honjo, Sumida, Tokyo 130, Japan.

CCC 0021-8995/88/010177-13$04.00

In our recent works, it has been shown that also the ionized membranes prepared through the plasma graft polymerization of acrylic acid[4] and methacrylic acid[5] performed the good permseparation of water with the higher permeation rates for the feeds with lower ethanol concentration. In the series of this work to develop the permselective membranes of water and ethanol, plasma graft polymerization was employed for the surface specific activation of the substrated by glow discharge plasmas. The activated surface of the substrate porous polypropyrene film was then graft polymerized by the monomers, and permselective membranes were prepared. Since the graft polymers which function as the permselective layer are bounded to the substrate film chemically, they are stable and insoluble to the solvents as long as the substrate is stable. In other words, one of the important characteristics of the plasma graft-polymerized membranes lies in the sharing of the functions; i.e., the permseparation and the mechanical strength are due respectively to the graft polymer layer and the substrate film. The ionizations of the grafted poly(acrylic acid) and the poly(methacrylic acid) on the permselective membranes resulted in the enchancement of the selective permeation of water.

By the way, in the acrylic acid and the methacrylic acid graft-polymerized membranes the carboxylic acid groups were fully ionized to carboxylates as confirmed by infrared spectra. In contrast to these, if the partial ionization of the membranes is possible, it should be useful to see the effects on the permselectivity in more detail. Therefore, for this purpose, the membranes which contained polyacrylate structures partially were constructed by the graft copolymerization of acrylic acid (AA) with acrylamide (AAm) onto the porous polypropyrene film, and, using the membranes with a different amount of the polyacrylate ions, water permselectivity from water–ethanol mixture solutions was investigated by pervaporation. The results were compared to the permseparations through the AA graft-polymerized and the AAm graft-polymerized membranes.

EXPERIMENTAL

Materials. Porous polypropyrene film with average pore size 2000 Å Celgard) was used for the substrate of permselective membranes. Acrylamide was purified by recrystallization from benzene–ethanol, and acrylic acid by distillation under reduced pressure.

Plasma Graft Polymerization. Procedure of plasma graft-polymerization was principally the same as described previously for the graft polymerization of acrylic acid and methacrylic acid.[4,5] The process and the apparatus used for graft polymerization are schematically represented in Figure 1. Plasma graft polymerization was performed by the two successive processes of the surface activation of the substrates and the followed polymerization of monomers onto the surface.

At first, the plasma surface activation was carried out as follows. Substrate porous polypropyrene film with the size 6×6 cm^2 was placed at the position (2) in the figure on the wall inside of the reactor (1), which was 240 mm in length and 30 mm in inner diameter, and the system was evacuated at the constant pressure about 2.7 Pa. Then the film was exposed to the glow discharge plasma of residual gas, generated at the frequency of 13.56 MHz at
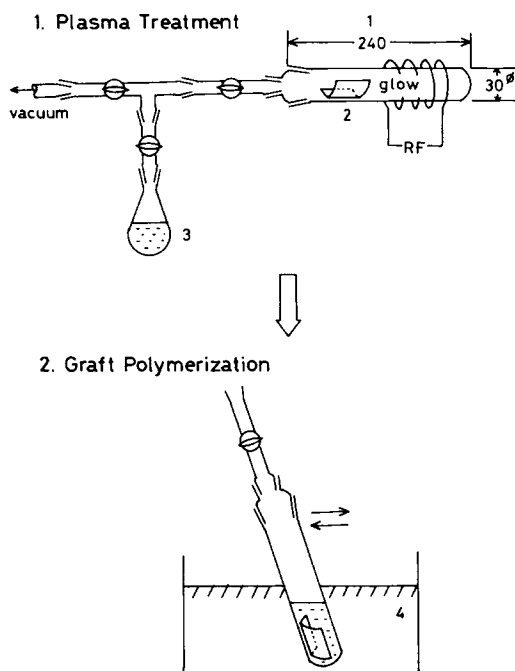
Fig. 1. Schematic representation of the procedure and the apparatus for plasma graft polymerization: (1) reactor; (2) position of substrate film; (3) monomer reservoir; (4) water bath.

10 W. In order to prevent the defects of the substrate by the etching of plasma, the milder plasma condition with a shorter period of 30 s was employed throughout this experiment.

Next, the graft polymerization of monomers was carried out as follows: About 30 mL of the 4% aqueous monomer solution was introduced under vacuum through the stopcocks from the monomer reservoir (3) to the reactor (1), and the substrate was put in contact with the monomer to initiate the graft polymerization. Monomer mixtures of AA and AAm with the ratios 0, 0.2, 0.4, 0.5, 0.6, 0.8, and 1.0 (= AA/AA + AAm) were reacted at 60°C with shaking in the water bath (4). After the polymerization was ended, the membranes were washed and soaked in distilled water overnight, and the residual monomers and the homopolymers were removed. Grafting was estimated by the weight increase after the graft polymerization in the dry states, and given in mg/cm^2.

Ionization of the Graft-Polymerized Membranes. Ionization was made by treating the membranes with the 2% aqueous sodium hydroxide solution at room temperature for about 20 min. Conversion of the AA copolymers to the acrylate was confirmed by infrared spectra; namely, the absorption peak at 1720 cm^{-1} for the stretching vibration of carbonyl was completely transferred to the position of 1560 cm^{-1}. Hydrolysis of the graft copolymerized AAm might not occur under the mild alkaline treatment condition, and this was deduced from the fact that the AAm graft polymerized membranes did not give the new peak at 1560 cm^{-1} for the hydrolyzed and ionized polyacrylate after the same alkaline treatment.

Pervaporation. The procedure of pervaporation was principally the same as described previously.[4,5] A membrane 4.7 cm in diameter was used and equipped in a stainless steel holder. Aqueous ethanolic solutions up to 90% were used, and the permseparation was examined. About 30 mL of the feed was supplied, and the other face of the membrane was evacuated at higher than 3.0 Pa under the blank conditions. During the pervaporation, the system pressure ranged from 10 to 130 Pa, depending on the permeation rates. The pervaporation experiments were usually carried out at 40°C in a water bath, and they were also made in the temperature range between 30 and 50°C to see the temperature dependences of permseparation. Activation energies for permeation were obtained from the Arrhenius plots.

Permeates were collected in a cold trap in liquid nitrogen. The flux was obtained from the weight and given in kg/m^2 h. Water and ethanol was analyzed with gas chromatography, and the concentrations were obtained from the peak strengths.

Permselectivity was evaluated from the separation factor, which was obtained by the concentrations of the two components in feed and in permeate. Separation factor of water (α_{EtOH}^{water}) was calculated from the following equation:

$$\alpha_{EtOH}^{water} = (X_{water}/X_{EtOH})/(Y_{water}/Y_{EtOH})$$

where X_{water} and X_{EtOH} are the concentrations of water and ethanol in the permeate and Y_{water} and Y_{EtOH} are those in the feed.

RESULTS AND DISCUSSION

Preparation of Permselective Membranes

Water–ethanol permselective membranes were prepared by the plasma graft polymerization and the followed ionization of the graft-copolymerized AA polymer layers. Suitable formation of the layer to fill the pores of the substrate film is necessary to perform the permseparation of liquids like water–ethanol as mentioned before.[4] Since the plasma graft polymerization is done by the two successive processes, i.e., the plasma surface activation of the substrate and the graft polymerization by the monomers, the grafting is naturally dependent on the reaction factors derived from the processes. Graft polymerization of AA and AAm alone onto porous polypropyrene film was previously described depending on the plasma pretreatment period, the temperature for grafting and so on.[4,5]

Figure 2 shows the results on the graft copolymerization of AA and AAm with the various mixing ratios onto the polypropyrene film substrate which was previously treated by the residual gas plasma at 10 W for 30 s. Graft polymerization was carried out in the 4% aqueous monomer solutions at 60°C for 1.0 and 2.0 h, respectively. It should be noticed that the monomer concentration is that of the added ones of the two monomers.

Throughout this study, the residual gas was used as a plasma source, which gave a pale blue color and was different from the red of air plasma. The plasma seemed to be mainly composed of hydrogen released from the surface
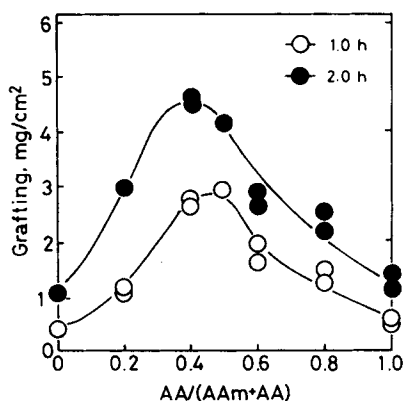
Fig. 2. Dependence of graft copolymerization of AA and AAm on the mixing ratio: (○) 1 h; (●) 2 h.

of the substrate by etching during the plasma exposures, judged by the glow. Indeed, the weight loss of the substrate polypropyrene film after the plasma pretreatment under the condition described above was negligibly small. It was thus presumed that the surface morphology of the porous film was not changed at this stage practically.

Both AA and AAm are reactive to give the graft polymers onto the porous polypropyrene film and the graft polymerization was remarkably increased when the mixtures were reacted. The maxima were observed at the AA mole ratio 0.4–0.5. The copolymerization behavior can be compared with other mixture systems like sodium styrenesulfonate–AAm.[4] When sodium styrene-sulfonate was reacted with AAm, the graft copolymerization did not take place practically as described before. Thus the graft polymerization is much dependent on the monomer combination.

It should be interesting to know how the monomer mixtures graft copo-lymerize and in what composition the polymer layer is formed. The quantitative analyses of the graft polymer layers were attempted by the infrared spectra, but enough information could not be obtained. However, it can be stated that the graft polymer formed reflects the composition of the starting monomer ratio in some manner, judging from permseparation behaviors which will be described later.

Water–Ethanol Permseparation

Water–ethanol permseparation through the copolymerized and the ionized membranes was evaluated by pervaporation. Figure 3 shows the dependences of the flux on the AA mixing ratio in the membrane, respectively, for the feeds with the ethanol concentration 0, 20, 50, 70, and 90%. It should be noticed here that the membranes as prepared in the Figure 2 were used for the pervaporation experiments.

Some characteristics can be pointed out. First, the flux decreased for both the neutral and the ionized membranes, as the ethanol concentration in feed increased from 0 to 90%. This is the common behavior in the water-permselec-tive membranes. In addition, the ionization of the graft copolymer layer with
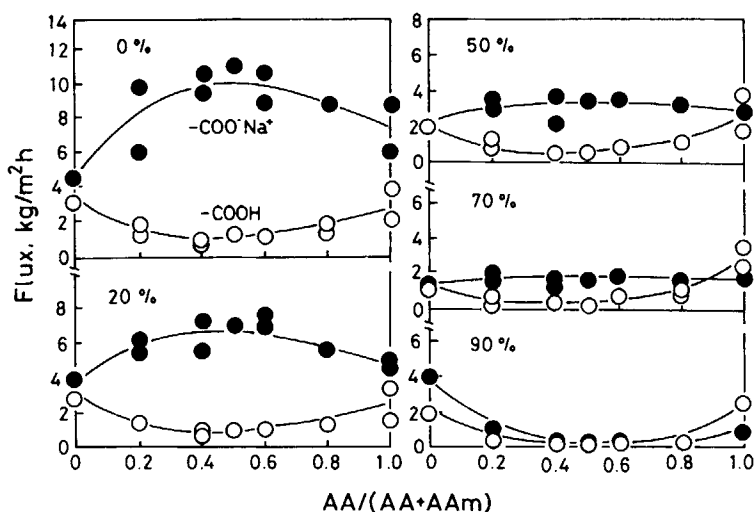
Fig. 3. Flux through the copolymeric membranes and the ionized membranes prepared with various AA mixing ratio.

the less mixing of AA was still effective for the permseparation of water. Minimum in the flux through the neutral membranes was observed in the range from 0.4 to 0.6 of the AA mixing ratio, while the maximum appeared in this range in the ionized state. The lower permeation rate in the neutral membranes was ascribed to the greater thickness, but it is quite interesting that the flux was rather high especially for the feeds with lower concentration of ethanol in the ionized state.

Permselectivity of water was naturally dependent on the state of the membranes. Figure 4 shows the dependences of the separation factor of water on the AA mixing ratio, respectively, for the feeds with 20, 50, 70, and 90% ethanol. The value of separation factor was in general greater in the ionized membranes, although they were smaller for the feed with 20% ethanol. The lower permselectivity for the 20% ethanol is related to the much higher permeation rate (as shown in Fig. 3). As the concentration of ethanol in feed increased, the separation factor increased and had a maximum around 70%. The effect of ionization on the permselectivity is again evident even for the lesser mixing of AA in preparing the membranes.

The results on pervaporation described above were for the membranes in which the membrane thickness or the grafting amount was not same. Then, the copolymers with the mixed AA ratio 0.4 were utilized, and the dependences of pervaporation on the grafting thickness were investigated. The membranes with various grafting up to 3.3 mg/cm^2 were prepared by changing the grafting period.

Figure 5 shows the results on the fluxes respectively for the neutral and the ionized membranes depending on the grafting amounts. As the grafting exceeded about 1.2 mg/cm^2, the permseparation became practically enhanced by suppressing the effusion of the water–ethanol feeds. In the neutral membranes, the flux was almost constant, independent of the grafting amount when more than 1.2 mg/cm^2. However, in the ionized membranes, the situa-
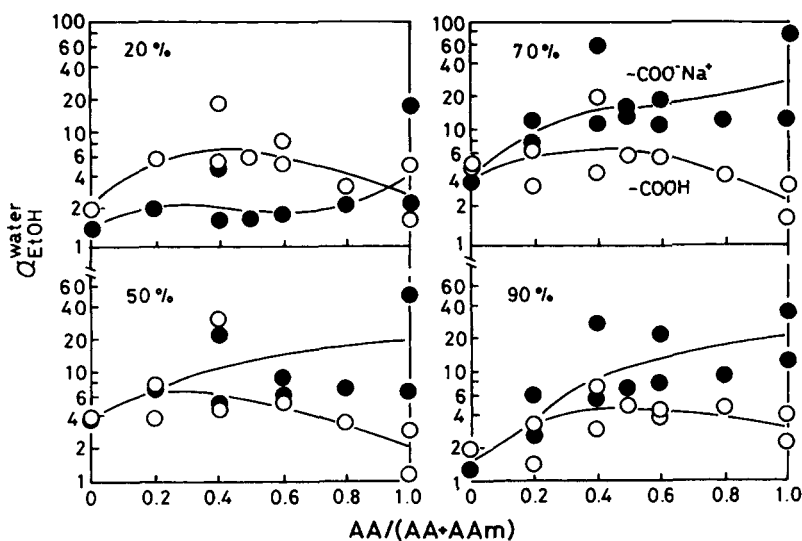
Fig. 4. Separation factor of water for the copolymeric membranes and the ionized membranes prepared with various AA mixing ratio.

tion was somewhat changed; namely, the flux increased with the grafting for the water-rich feeds, while that decreased for the feeds with the higher ethanol concentration than 50%. The phenomena indicate the effect of the solvents on the state of the graft polymer layer which acts as the permseparation. In other words, the higher ethanol feeds make the hydrophilic graft polymer layer shrink to reduce the permeation.

When the pervaporation experiments were carried out with the membranes which were graft-polymerized less than 0.6 mg/cm^2 using the 90% ethanol feed, the fluxes were extremely high in both the neutral and the ionized
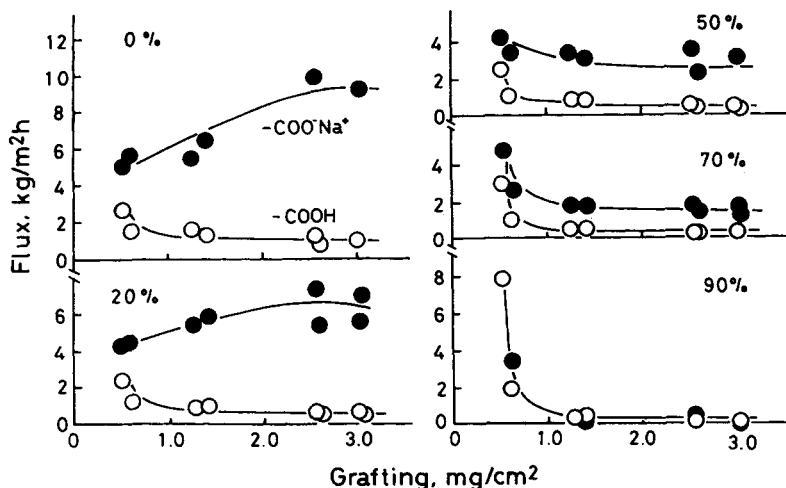

Fig. 5. Dependence of flux through the copolymeric membranes (AA/AA + AAm = 0.4) on the grafting thickness.

membranes, and the permseparation of water did not take place practically. This is probably due to the formation of the macropores along the pores in the substrate film, owing to the mechanochemical shrinkage of the graft polymers in contact with the feed ethanol-rich solutions. This results in the effusion of the mixture feed solutions.

It should be noticed here that the permeation rates did not reciprocally decrease with the increase of the grafting or the membrane thickness. This is quite different from the behaviors observed in other membrane separation processes like gas separation. The phenomena are closely related to the permeation mechanism by pervaporation which is performed through the change of phases from liquid to gas. In pervaporation, the permeation is mainly regulated by the skin layer which is tight at the vacuumed face of the membrane, and the residual swelled portion of the membrane acts for the selective adsorption of a component in feed. Thus the thickness of the permselective membrane does not necessarily work on the permeation rate proportionally.

Next, the dependences of the separation factor of water on the grafting thickness were investigated, and the results for the feeds with 20, 50, 70, and 90% ethanol are shown in Figure 6, respectively, for the neutral and the ionized membranes. The results also suggest that the permseparation of water becomes effective with the membranes prepared by the grafting more than 1.2 mg/cm^2. It should be noted that the permselectivity became almost constant when the membranes were graft-polymerized enough, and this should be preferable for the practical application.

The maximum value of separation factor was 62.1 for the 67.0% ethanol feed in the ionized state of the copolymeric membrane prepared with the 0.4 mol ratio and AA (grafting, 2.61 mg/cm^2) in the range investigated in this study.
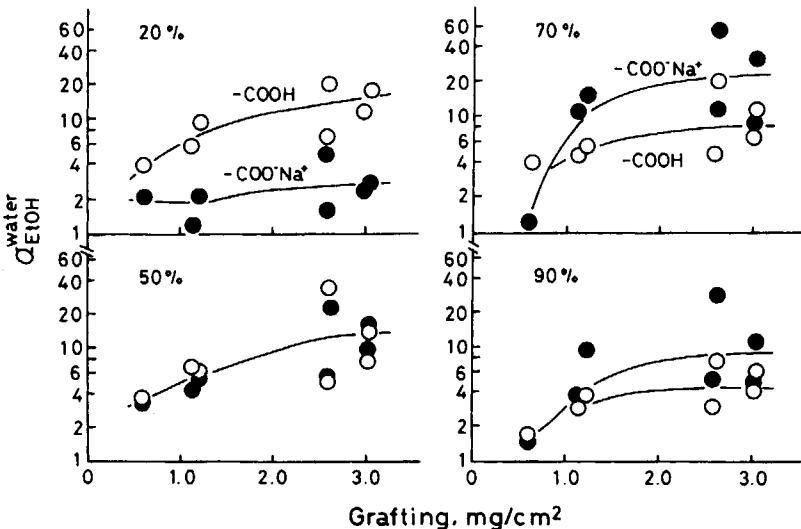

Fig. 6. Dependence of separation factor of water for the copolymeric membranes (AA/AA + AAm = 0.4) on the grafting thickness.

The results can be comparable to that obtained with the AA graft-polymerized and ionized membranes.[4]

The above results were all obtained by the experiments carried out at 40°C. Some experiments were also made in the temperature range from 30 to 50°C, and the temperature dependences of pervaporation were investigated. Figure 7 shows the Arrhenius plots of permeation through the graft copolymeric membranes prepared with the AA ratio 0.4 (grafting, 2.61 mg/cm^2), respectively, in the neutral and the ionized states. It is observed that the slope of flux is smaller for the ionized membranes, and then the temperature dependences are much less. In other words, the decrease of flux is depressed at a lower temperature. From the slopes, the activation energy of permeation was calculated, and the value was about 9.1 kcal/mol for water in the neutral membrane. The energy was much smaller in the ionized membrane, and lay between 4.2 and 5.5 kcal/mol for these feeds. The value of the activation energy obtained in this study may not be so strict because of the limited data of flux, but the trends that the energy is reduced in the ionized membranes are free from doubt.

The separation factor was slightly decreased as the temperature increased. The phenomena observed during the investigation of the temperature dependences suggest that the higher pervaporation performances could be obtained in the ionized membranes without so much depression of the permeation rates. This should be the crucial merit of the ionized membranes, as they can be effectively utilized even under the lower temperature conditions without consuming much heat energy.
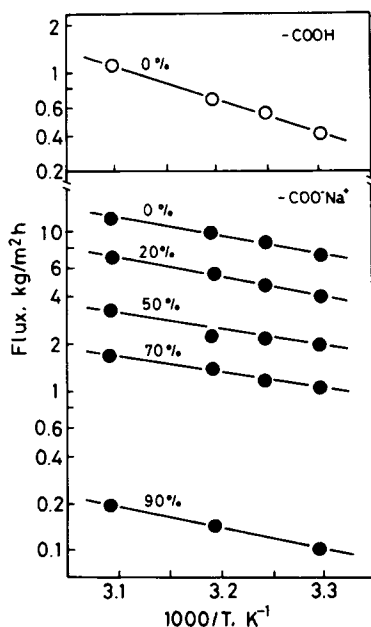

Fig. 7. Arrhenius plot of flux through the copolymeric and the ionized membranes (AA/AA + AAm = 0.4, grafting = 2.61 mg/cm^2).

Usually the higher separation factor results in the lower permeation rate. Then, the permseparation cannot be evaluated only by the separation factor, but the permeation rate should also be taken into account. According to this idea, Nakagawa has suggested that the efficiency of the permselective membranes should be judged from the relationships of the two factors: for example, by the products of the separation factor (α) and the flux (Q), i.e., αQ^6. The membrane with the higher value of αQ should be then really good.

The relationships between the separation factor and the flux were taken by the logarithmic values. The results are shown in Figure 8, for the copolymeric membranes prepared with the 0.4 mol AA mixing and for the ionized membranes. The relations were compared with those for the AA graft polymers and for the AAm graft polymers. They are shown in Figures 9 and 10, respectively. The data were collected from the various membranes with different grafting, and from the different experimental conditions of temperature.

The fluxes and the separation factors are related to each other as shown by the solid lines in the figures. Average αQ values were calculated from each of the data, and the results are shown with the broken lines. With the neutral membranes, the values did not exceed 10 (kg/m^2 h), and they are more or less the same among the three types of membranes. In the AA–AAm copolymeric membranes, the higher value of the separation factor was obtained in general; but the fluxes were lower, and as a result the αQ values became similar to the other two. When the membranes were ionized, the values were extremely increased and became greater by more than 10 times in some cases, although
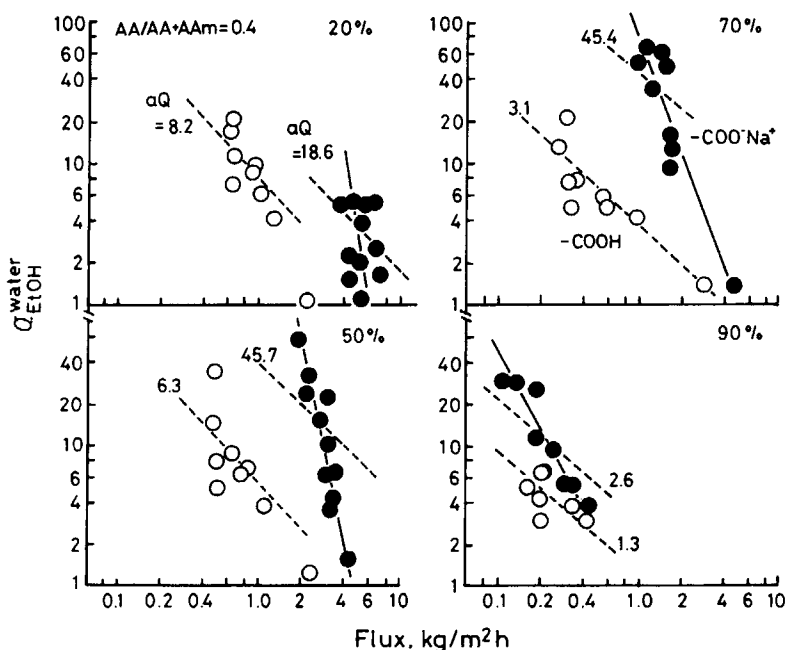

Fig. 8.   Relationships between the separation factor of water and the flux for the plasma graft copolymerized membranes of AA and AAm (AA/AA + AAm = 0.4) and the ionized membranes.
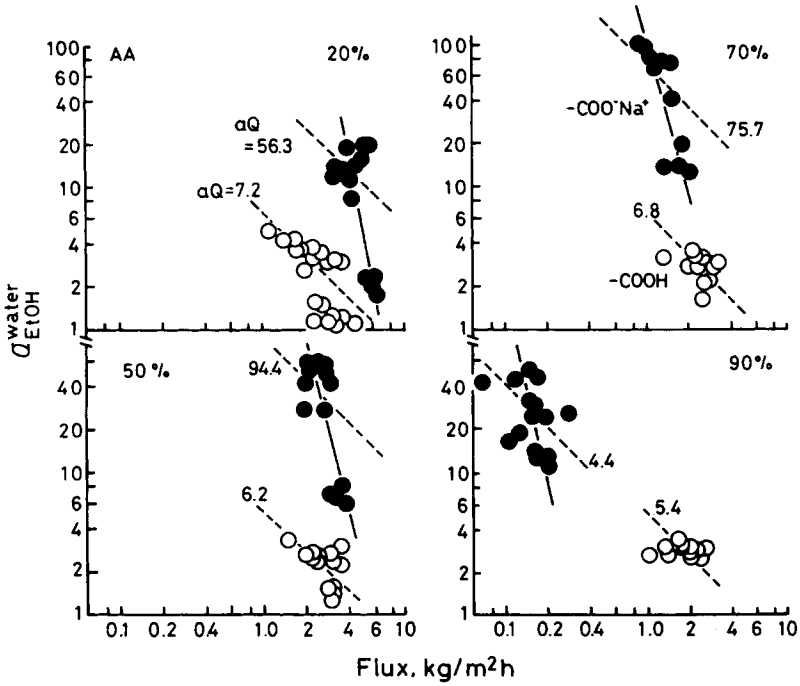
Fig. 9. Relationships between the separation factor of water and the flux for the plasma graft-polymerized membranes of AA and the ionized membranes.
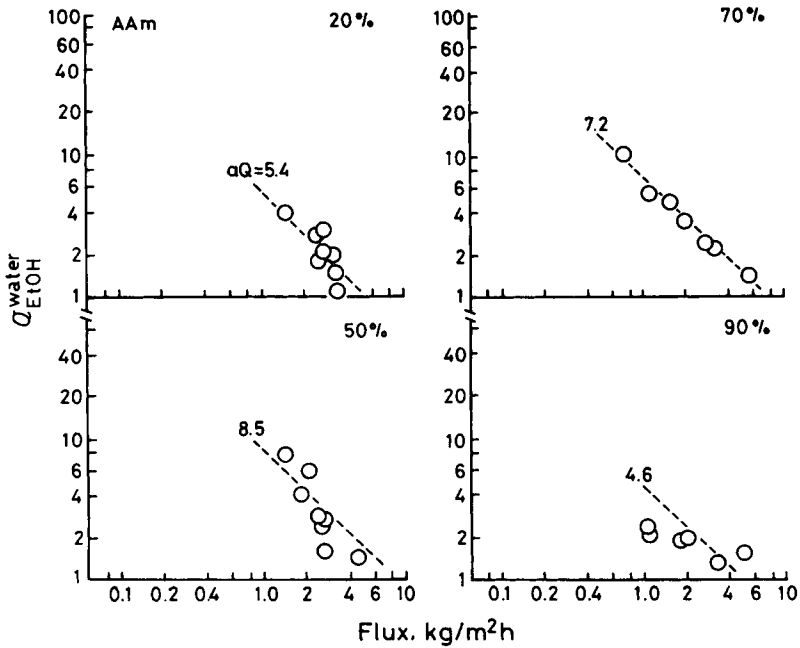

Fig. 10. Relationships between the separation factor of water and the flux for the plasma graft-polymerized membranes of AAm.

TABLE 1
Comparison of the Water–Ethanol Permselectivity by Pervaporation in the Ionic Membranes

Membrane	EtOH (%)	Temp. (°C)	α_{EtOH}^{water}	Flux (Q) (kg/m² h)	αQ	Ref.
Nafion[a]–Cs$^+$	78.3	29	10.4	0.180	1.87	1
Nafion–K$^+$	78.5	29	8.4	0.264	2.22	1
AMV[b]–SO$_4^{2-}$	97	60	70	0.083	5.81	2
AMV–OH$^-$	93	60	53	0.383	20.3	2
AMV–SCN$^-$	85	60	38	0.467	17.7	2
AMV–Cl$^-$	80	60	27	0.833	22.5	2
g-AA$^-$Na^{+c}	20	40	19.3	4.83	93.2	4
	50	40	51.2	2.66	136.2	4
	70	40	79.8	1.10	87.8	4
	90	40	29.7	0.17	5.05	4
g-AAm-AA$^-$Na^{+d}	34.6	40	19.7	3.39	66.8	This work
	44.7	40	24.4	2.31	56.4	This work
	54.6	40	42.4	1.98	84.0	This work
	67.0	40	62.1	1.39	86.3	This work
	76.7	40	46.8	0.60	28.1	This work
	88.5	40	29.7	0.14	4.16	This work

[a] Hollow fiber; E. I. DuPont de Nemours & Co.
[b] Anion exchange membrane; Asahi Glass Co.
[c] Plasma graft-polymerized membrane of AA; grafting = 1.26 mg/cm².
[d] AA/AA + AAm = 0.4; grafting = 2.61 mg/cm².

they were somewhat smaller than those for the ionized membranes of AA grafting.

In Table 1, some typical data for the water–ethanol permseparation by pervaporation through ionic membranes are collected from literature, and compared with those obtained in the study. Superiority of the graft-polymerized and ionized membranes is obvious from the comparison. The results shown for the ionized membrane obtained in this study are indeed the best ones. The average αQ values are also greater as presented in Figure 8.

In the ionized copolymeric membranes having the similar permselectivity to that of the AA polymerized membranes, the higher αQ is attributed to the higher fluxes. However, when the ethanol concentration in feed is higher than 88%, the flux becomes extremely low, resulting in the lower αQ values.

CONCLUSION

Partially ionized membranes in the form of polyacrylate were prepared through the graft copolymerization of AA with AAm onto the porous polypropyrene film which was previously treated by glow discharge plasma, and the permseparation of water from the water-ethanol mixtures was investigated by pervaporation. From this study, the following important aspects were found.

1. Grafting was remarkably increased by the copolymerization of AA and AAm, and the polyacrylate was incorporated partially on the permselective membranes.

2. Higher permseparation of water was obtained with the ionized membranes when the ethanol concentration in feed exceeded 50%, and the effects

were observed even in the smaller mixing ratio of AA at 0.2 in preparing the membrane.

3. In the copolymers of AA with the mixing ratio of 0.4, the flux was not so high as those for the AA and AAm copolymeric membranes, but that was greatly improved by ionization and gave almost the same flux with those by the ionized membranes of AA graft polymers. The separation factor was also improved.

4. In the ionized membranes, the decrease of flux at a lower temperature was much depressed compared to the neutral membranes, and as a result, the activation energy of permeation was much smaller, lying between 4.2 and 5.5 kcal/mol.

5. Permseparation was evaluated by the products of α and Q. The value was remarkably increased by ionization more than 10 times in some cases, although somewhat smaller than those for the ionized membranes of AA graftings.

References

1. I. Cabasso and Z.-Z. Liu, *J. Membr. Sci.*, **24**, 101 (1985).
2. A. Wenzlaff, K. W. Böddeker, and K. Hattenbach, *J. Membr. Sci.*, **22**, 333 (1985).
3. M. Yoshikawa, T. Yukoshi, K. Sanui, and N. Ogata, *Polym. Prepr., Jpn.*, **34** (3), 401 (1985).
4. T. Hirotsu, *J. Appl. Polym. Sci.*, **34**, 1159 (1987).
5. T. Hirotsu, *Ind. Eng. Chem. Res.*, **26**, 1287 (1987).
6. T. Nakagawa, *Hyomen (Surface)*, **18**, 475 (1980).