# 수팽윤성 고분자막을 통한 용질의 투과특성 : Ⅱ. Copoly(acrylonitrile–acrylic acid)막의 투과성

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# Permeation Characteristics of Solutes through Water Swollen Polymeric Membranes : II. Copoly(acrylonitrile–acrylic acid) Membranes

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**Abstract** : Emulsifier–free polymerization of acrylonitrile and acrylic acid in the aqueous medium was performed, and the various copolymer latex membranes were prepared. The transport behavior of various solutes through water swollen membranes has been studied for hemodialysis. The results showed that the permeabilities of copolymer membranes are higher than that of Cuprophane and the solute permeability is greatly dependent on the water content of membrane. The membrane properties were considerably influenced by water content. Namely, hydrophilic portion, acrylic acid content in the membrane affects the solute permeation, mechanical properties, microstructures of membrane, and water binding properties, etc. Water structures in the copolymer membranes were investigated by differential scanning calorimetry, and the relative amounts of bound and free water in various membranes were determined. The content of free water increased with the increase of acrylic acid content. From the result, it is evident that the free water facilitates the solute permeation through the membrane. The microstructures of latex membranes were studied by scanning electron microscopy, and the clustered particles were observed.

## INTRODUCTION

The modern artificial kidney was first studied by Kolff, et al. using Cellophane tubing which was wound around a drum and thereafter, various types of membrane modules and machines have been developed. Nowadays, Cuprophane as a sort of cellulose derivatives is widely used and many effective membrane modules like a hollow fiber membrane were invented. Then, for the purpose of minimizing the apparatus many researchers[1~3]

are developing high performance membranes which have effective dialyzing rate and better mechanical strength.

Emulsifier–free polymerization of vinyl monomers in aqueous medium were reported by many authors.[4~6] Emulsifier–free polymer latexes were frequently researched because of their improved film forming properties. And they also will be able to be used in medical applications because of their purity without emulsifier.

In this study, acrylic acid and acrylonitrile

were copolymerized in emulsifier-free aqueous medium. Their physical properties and permeation characteristics were studied, and especially, the applications for artificial kidney membranes were investigated. The technique of hemodialysis consists of taking blood outside of the body, enclosing it in a semipermeable membrane, and then putting into the other side of membrane a dialyzing solution which will remove urea and other blood toxins. In order to evaluate the performance of removal of blood toxins, transport behavior of various solutes through water swollen copoly(acrylonitrile-acrylic acid) membranes has been studied at 38℃. And the thermograms of differential scanning calorimetry for water swollen membranes were measured in order to clarify the relation between the solute permeability and water structure in the copolymer membranes. In addition, scanning electron microscopy was also used to observe the cross-sectional structures of water swollen latex membranes.

## EXPERIMENTAL

### Materials

Acrylonitrile(Kanto Chemical Co.) and acrylic acid(Kokusan Chemical Works) were distilled under reduced pressure. Deionized water was used for solvent medium in polymerization. Potassium persulfate(Kanto Chemical Co.) was purified by recrystallization. Sodium bicarbonate(Wako Pure Chemicals) was used without further treatment.

### Copolymerization

Copolymerizations of acrylonitrile and acrylic acid were carried out in an emulsifier-free aqueous medium with varying monomer feed ratio at 70℃. Polymerizations were carried out in a 500ml flask fitted with a mechanical stirrer and an inlet tube of nitrogen gas.

Acrylonitrile and acrylic acid were added to deionized water at 70℃ and the solution was adjusted to pH 6 by sodium bicarbonate. After the monomer solution was stabilized, potassium persulfate was added, and then the concentration

of initiator was 0.005 mole/l. After 2 hours passed, latex particles were precipitated by adding dil-HCl. Precipitated polymers were purified, residual monomers being removed by extraction with water and benzene for 24 hours. Obtained polymers were dried at 50℃ in a vacuum oven to constant weights and identified by FTIR(Nicolet model-5DX). And the composition was also calculated by use of elementary analysis with comparing the nitrogen and oxygen contents in copolymers.

### Membrane Preparation

The membranes were prepared as flat sheet form by solvent casting method. The casting solution used in this experiment was prepared by resolving polymer in dimethyl formamide as a concentration of 7 wt.%. The polymer solution was cast on a glass plate using a Gardner knife with a thickness of 380 $\mu$m and dried in a vacuum oven at 60℃ for 10 hours. The glass plate with the membrane was immersed in distilled water for 30 minutes and then, membrane was removed from the glass plate. And all the membranes were swollen in distilled water for 7 days at 38℃ before subsequent use. The thickness of these water swollen membranes ranged from 35 to 190 $\mu$m.

### Water Content

Membranes were swollen in distilled water for 7 days at 38℃. They were then taken, blotted with filter paper, and weighed. They were then dried in vacuum oven at 60℃ for 10 hours. After the weight of dried membrane reached a constant value, the water lost from the membrane was calculated from the weight loss. This was the wet weight of the membrane. The water content was determined by the following equation :

$$\text{Water content}(\%) = (W_1 - W_0)/W_1 \times 100$$

where $W_0$ is the weight of dried sample and $W_1$ is the weight in fully swollen state, respectively.

### Mechanical Properties in Wet State

Tensile strength and elongation of the me-

mbranes in wet state were measured by Instron type universal testing machine(Toyo Baldwin UTM-4-100). Every membrane with 5mm width and 40mm length was used for measurement after fully swollen in distilled water at 38℃. Testing conditions included a cross head speed of 5mm/min, a 500g full scale load, and a initial span length of 10mm.

### Dialysis Rate Measurement

The permeabilities of various solutes were measured using a batch type dialyzer made of poly (methyl methacrylate) and its feature is shown in Fig. 1. The useful volume of each compartment is approximately 100ml and it is equipped with a water bath and mechanical stirrer. The effective membrane area is 7.07cm².

The membrane was fixed in a two-part silicone rubber ring. The compartments were filled with aqueous solution in one side of the membrane and distilled water in the other side. The concentrations of aqueous solutions used in this experiment were as follows : urea 200ppm, creatinine 200ppm, dextrose 1,000ppm and sucrose 1,000ppm. The solution of each compartment was agitated as efficient as possible to minimize the concentration polarization on the surface of membrane.

During the dialysis, samples of $100\mu l$ were taken from diluent compartment and then concentration was measured by HPLC, concentration of solute was determined as a function of time

at 38℃ and the solute permeability coefficient P was calculated from the following equations[8] :

$$P't = \frac{1}{(1/V_1 + 1/V_2)} \ln \left( \frac{1 - C_2/C_1}{1 + V_2C_2/V_1C_1} \right) \quad (1)$$

$$P = P'\Delta x/A \quad (2)$$

where

$V_1$, $V_2$ : volumes of the concentrate and the diluent compartment(cm³)

$C_1$, $C_2$ : concentrations of compartments at time t(sec)

$\Delta x$ : membrane thickness(cm)

$A$ : effective membrane area(cm²)

$P'$ : apparent permeability coefficient(cm³/sec)

### Water Permeability Measurement

The measurement of water permeability of membrane is carried out by using an Amicon Ultrafiltration cell(Amicon model-8050) with an effective membrane area of 13.4 cm². A schematic representation of the apparatus is shown in Fig. 2.

The permeation cell is immersed in an water bath controlled with a thermocouple at 38℃. Water permeability was measured at a pressure of 0.5 atm using compressed nitrogen gas. The volume of permeated water was measured as a function of time. Samples of permeated water were taken and weighed until steady state fluxes were obtained. The water permeability coefficient
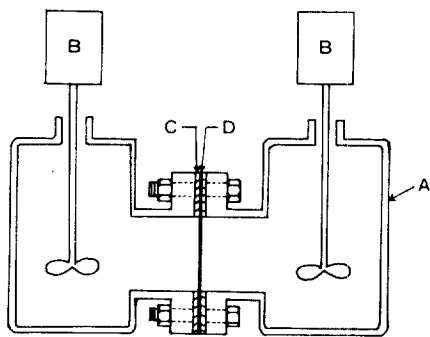


Fig. 1. Apparatus for solute permeability measurement(A : PMMA compartments, B : mechanical stirrer, C : sealing rubber, D : membrane)
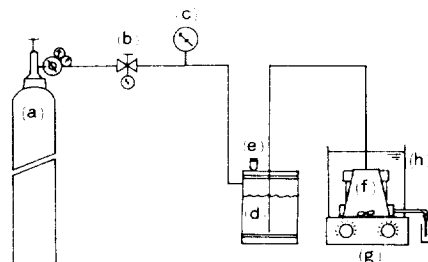


Fig. 2. Schematic diagram of water permeation apparatus. (a)N₂ bomb, (b)air pressure controller,(c)pressure gauge,(d)reservoir, (e)safety valve, (f)permeation cell (g)hot plate & magnetic stirrer, (h)water bath.

$K(cm^2)$ was calculated from following equation :

$$K = V \cdot \eta \cdot \Delta x / \Delta t \cdot A \cdot \Delta p \qquad (3)$$

where

V : volume of water transported($cm^3$)

$\eta$ : viscosity of water(dyne $\cdot sec/cm^2$)

$\Delta p$ : pressure difference(dyne $/cm^2$)

Water fluxes, $Jw \cdot \Delta x$ were also measured in the pressure range of 0.5–5 atm, and they were calculated from the following equation :

$$Jw \cdot \Delta x = Q \cdot \Delta x / A \cdot t(mole \cdot cm/cm^2 \cdot sec) \quad (4)$$

where Q is the moles of permeated water.

### Scanning Electron Microscopy

The cross–sectional structures of water swollen membranes were examined with a scanning electron microscope. Cross–sections were obtained by fracturing the membranes in the liquid nitrogen. And then, the membranes were freeze–dried over night and coated with gold.

### Differential Scanning Calorimetry

The melting endotherms of water in the copolymer membranes were measured by differential scanning calorimeter(Daini Seikosha model–SSC/560). The fully swollen latex membranes were wiped with a filter paper and then sealed in aluminum pans. The sample pans were cooled to −40°C and then heated in the stream of nitrogen gas at a program rate of 5°C/min to 20°C. The DSC was calibrated by using indium and distilled water as standards. The areas of melting peaks were measured and the amount of free water was computed. The amount of bound water was taken as the difference between the total water content and the content of free water.

## RESULT AND DISCUSSION

### Characterization of Copolymers

Copolymerization mechanism of styrene with acrylamide was previously reported by Kawaguchi, et al.[7] They showed that the reaction course was divided into three stage polymerization course : first stage, polymerization of acrylamide in the aqueous phase ; second stage, polymerization of styrene in the particles : and the third stage, polymerization of residual acrylamide in aqueous phase. Namely, competitive reactions of these monomers are dependent on the hydrophilic/hy-
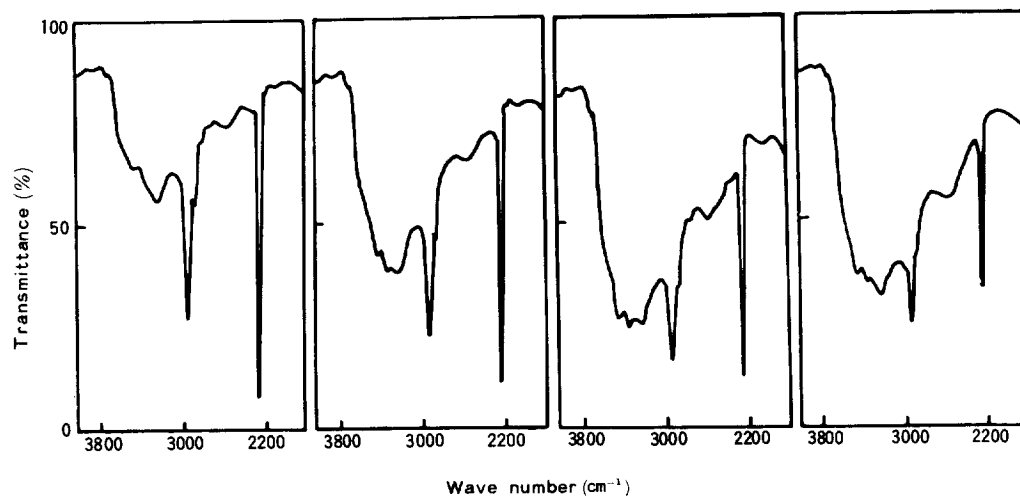


Fig. 3. IR spectra of Copoly(acrylonitrile–acrylic acid) membranes ; (A)PANAA–1, (B)PANAA–2, (C)PANAA–3, (D)PANAA–4

drophobic conditions of monomers and reaction medium. In this study, copolymerization of acrylonitrile with acrylic acid also should resemble the three stage mechanism.

Synthesized copolymers were identified by FTIR and corresponding features were shown in Fig. 3. Infrared spectra of copolymers have major adsorptions at about 3,200–3,600 cm$^{-1}$(–OH peak) and 2,243cm$^{-1}$(–CN peak). According to the increase of acrylic acid content in copolymer, the adsorption band of the –CN bond is clearly reduced in intensity and that of the –OH bond is broadly increased.

Compositions of copolymers were measured by elementary analysis and their results were given in Table 1. Oxygen atom belongs to only acrylic acid and nitrogen atom belongs to only acrylonitrile, respectively. Therefore, mole fractions of acrylic acid and acrylonitrile in copolymers were determined by comparing the contents of nitrogen and oxygen.

## Mechanical Properties of Membranes

Tensile strength and elongation of copolymers were measured with membranes swollen in distilled water at 38℃. Mechanical properties of membranes in wet state are shown in Table 2. As the content of acrylic acid in copolymer increased, tensile strength decreased greatly, nevertheless, elongation increased with a range of 95～470 %. Fully swollen copolymer membranes were lengthened like gum when they were strained. The variations of mechical properties with the mole fractions of acrylic acid in copolymers are given in Fig. 4.

Table 1. Elementary Analysis of Copolymers and Mole Fractions of Acrylic Acid in Copolymers

| sample | elementary analysis(%) | | | | mole fraction of acrylic acid |
|---|---|---|---|---|---|
| | N | C | H | O | |
| PANAA–1 | 22.85 | 64.16 | 5.47 | 6.11 | 0.10 |
| PANAA–2 | 20.90 | 61.69 | 5.70 | 9.56 | 0.17 |
| PANAA–3 | 18.84 | 58.52 | 5.93 | 16.99 | 0.28 |
| PANAA–4 | 14.49 | 54.55 | 6.00 | 23.06 | 0.41 |

Table 2. Mechanical Properties of Copoly(acrylonitrile-acrylic acid) Membranes

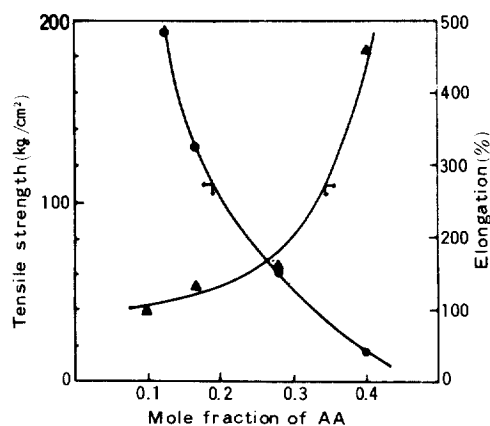| membrane | water content (wet base)(%) | tensile strength (kg/cm$^2$) | elongation (%) |
|---|---|---|---|
| PANAA–1 | 18 | 194 | 95 |
| PANAA–2 | 43 | 130 | 133 |
| PANAA–3 | 65 | 60 | 150 |
| PANAA–4 | 73 | 18 | 470 |



Fig. 4. Effect of the mole fraction of acrylic acid in copolymer on the mechanical properties of copoly(acrylonitrile–acrylic acid) membranes in wet state.
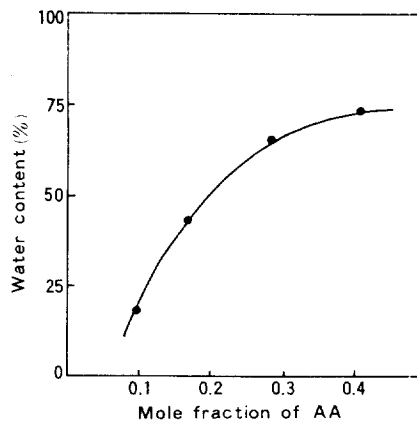


Fig. 5. Dependence of the water content at 38℃ on the mole fraction of acrylic acid in copolymer in copoly(acrylonitrile–acrylic acid) membranes.

Table 3. Solute Permeabilities of Copoly(acrylonitrile-acrylic acid) Membranes

| membrane | water content (%) | permeability of solute(cm²/sec) × 10⁷ | | | |
|---|---|---|---|---|---|
| | | urea | creatinine | dextrose | sucrose |
| PANAA-1 | 18 | 1.09 | 0.46 | 0.23 | 0.14 |
| PANAA-2 | 43 | 7.09 | 2.42 | 1.04 | 0.58 |
| PANAA-3 | 65 | 23.80 | 10.93 | 3.54 | 1.28 |
| PANAA-4 | 73 | 42.51 | 22.41 | 13.32 | 9.85 |

Mechanical properties of Cuprophane PT-150 membrane[8] were reported as follows : tensile strength, 30kg/cm² and elongation, 155% in wet state, respectively. Therefore, synthesized copolymer membranes have good mechanical properties compared with Cuprophane PT-150 membrane which is commonly used for hemodialysis in recent years.

Water contents were also measured to evaluate the effect of water on the permeation of solutes through water swollen membranes, and results are shown in Fig. 5.

**Permeation Characteristics of Solutes**

In order to evaluate the performances of membranes for the removal of uremigenic agents, dialyses were performed. Used solutes are urea (MW : 60), creatinine(MW : 113), dextrose(MW : 180) and sucrose(MW : 342). The results of solute permeation experiments are listed in Table 3.

In the case of Cuprophane PT-150 membrane, permeabilities[9] of various solutes are as follows : urea, $4.8 \times 10^{-7} cm^2/sec$. dextrose, $3.2 \times 10^{-7} cm^2/sec$ and sucrose, $1.95 \times 10^{-7} cm^2/sec$. PANAA-3 and PANAA-4 membranes have better permeabilities than Cuprophane PT-150 membrane. And the permeability coefficients of PANAA-2 membranes are somewhat similar to those of Cuprophane PT-150 membrane. In the case of PANAA-4 membrane, its permeability is very excellent, but it will not be able to be used for hemodialysis membrane because of its poor mechanical strength. Therefore, it is expected that the PANAA-3 membrane is the most suitable to the hemodialysis among prepared membranes.

For the PANAA membranes, the permeability data P of various solutes are plotted against the mole fractions of acrylic acid in Fig. 6. It is revealed that the solute permeabilities increase gradually with the mole fraction of acrylic acid.

As was previously shown in Fig. 5, water content increases with the mole fraction of acrylic acid because of its hydrophilicity. So to speak, solute permeability depends on the water content of membrane. Fig. 7 illustrates the dependence of the solute permeability on the water content.

Solute permeability increased with the water content almost linearly. But when the water content became more than about 60%, permeability coefficients of dextrose and sucrose increased abruptly. Generally, molecular weight of solute influences on the permeability of membrane. That
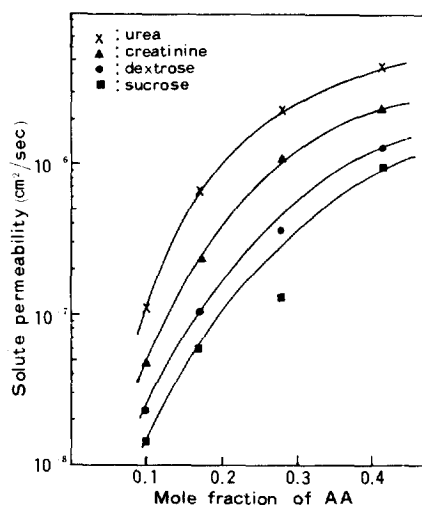


Fig. 6. Dependence of the solute permeability at 38℃ on the mole fraction of acrylic acid in copolymer in copoly(acrylonitrile-acrylic acid) membranes.

is to say, large molecule diffuses difficultly through the membrane compared with small molecule. Water soluble solutes diffuse through the membrane via water pockets of clustered water.[10,11] And water pocket has intimate relation with water content. If the water content of membrane inc-



Fig. 7. Dependence of the solute permeability at 38℃ on the water content in copoly(acrylonitrile-acrylic acid) membranes.



Fig. 8. Solute permeabilities of different molecular weight substances at 38℃ for copoly(acrylonitrile-acrylic acid) membranes.

rease to some extent, then water pocket is expanded largely and solutes diffuse through the membrane easily. In the case of large water content region in Fig. 7, solutes permeate easily and therefore, permeability is not greatly dependent on the molecular weight of solute.

Fig. 8 shows the dependence of the solute permeability on the molecular weights of various solutes. It can be seen that the decrease in permeability of PANAA–4 membrane as a function of molecular weight is less steep than those of the other PANAA membranes. It is consistent with the result of Fig. 7.

**Water Structures in the Copolymer Membranes**

As the acrylic acid content in the copolymer increases, the permeabilities of solutes in aqueous solution increase. Previous chapter, this phenomenon was discussed and we pointed that the permeability of solute is greatly influenced by water content of membrane. As discussed by other researchers,[12~14] permeabilities of non-ionic solutes through polymeric membranes are affected by the water content, and it is clear that the water content increases with the hydrophilicity of material. Consequently, the permeabilities of non-ionic solutes increase with the increase of hydrophilicity of material.

In the previous paper[15], we have described the interactions between blood and water swollen membranes. And it was considered that the water plays an important role in blood compatibility for the hydrophilic polymers. Blood compatibility is also required for the hemodialysis membranes. Ikada[16] reported that the nature of water greatly influences the blood compatibility and water like free water is very desirable.

As the water is imbibed in the membrane, hydrogen bonding between water and functional group of membrane is formed. And the solute permeability is influenced by water structure in the membrane. Many researchers[17~20] have reported the existence of considerable amount of bound water and characterized the behaviors of water in the water swollen membranes. The use of differential scanning calorimetry enables a qu-
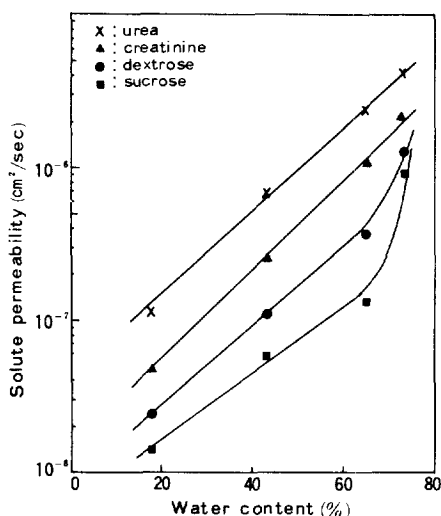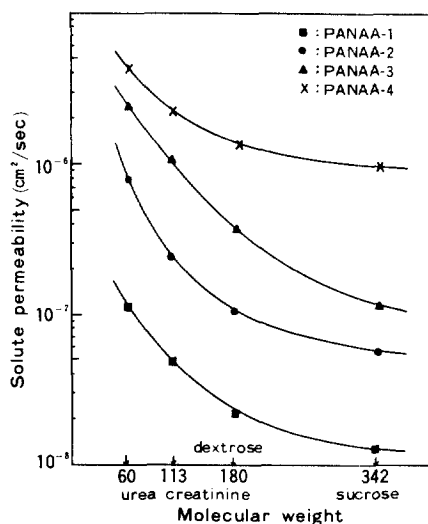
antitative determination of the relative amounts of bound and free water to be made.

Typical melting endotherms of water in co-polymer membranes and pure water are shown in Fig. 9. From the thermogram, the amounts of bound water and free water were calculated and the results are given in Table 4. As a result, it is revealed that PANAA-1 membrane has no free water and free water content increases with the increase of acrylic acid content.

Although free water is associated and hydrogen bonded with each other, its bonding force is very weak compared with that of bound water, and bound water may be immobile. For this reason free water enables the solutes to pass through the membrane easily.
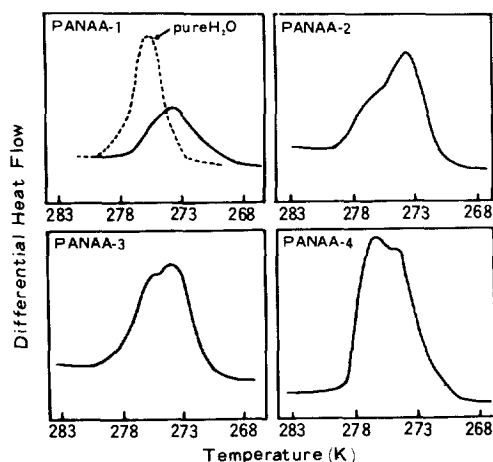


Fig. 9. DSC melting endotherms of water in copoly (acrylonitrile–acrylic acid) membranes and pure water.

The solute permeability of PANAA-4 membrane increases abruptly because of the large amount of free water. In the case of PANAA membranes, moderately polar groups such as –COOH exist and influence the hydrogen bonding between water and membrane. Then, they effectively compete with the tendency of water molecules to associate with others of their kind.[21] Therefore, destructuring of water complexes occurs and facilitates the solute permeation through the membrane.

**Morphology of Copolymer Membranes**

In order to discuss the relation between the solute permeability and morphology of the membrane, cross–sectional structures were observed by scanning electron microscope and the appearances were shown in Fig. 10.

Microstructures of these membranes were quite similar to those of PVA–AN,[22] PVA–AN–HEMA[23] graft copolymer latex membranes prepared by Ohtsuka, et al. They explained the location of hydrophilic/hydrophobic component and the formation of latex particles clustered in the graft copolymer latex membranes.

In the pictures of various PANAA membranes, clustered particles were observed. As the acrylic acid content increased, particle size increased, and besides, the gap between particles appeared to be clear. In this case, it is suspected that poly-acrylonitrile and polyacrylic acid components are located in the particles as a two phase strucutre. Hydrophobic polyacrylonitrile component forms the nuclear portion of particle, and hydrophilic

Table 4. Water Contents and Distributions of Bound and Free Water in Copoly (acrylonitrile-acrylic acid) Membranes

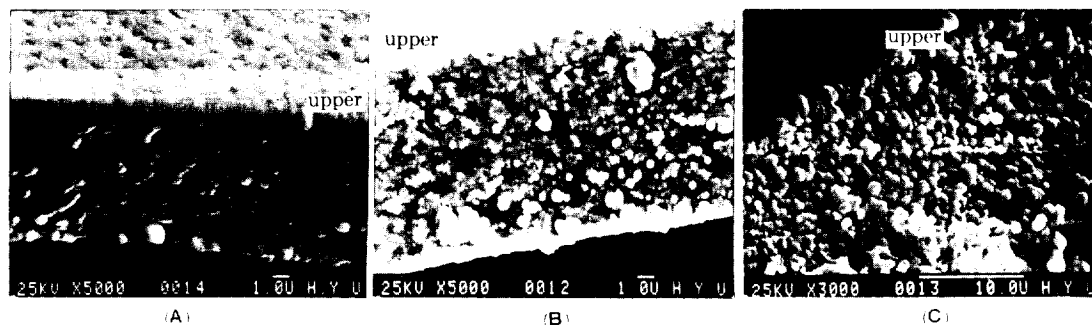| | PANAA–1 | PANAA–2 | PANAA–3 | PANAA–4 |
|---|---|---|---|---|
| total water content(%) | 18 | 43 | 65 | 73 |
| free water content(%) | 0 | 15.9 | 27.3 | 33.6 |
| bound water content(%) | 18 | 27.1 | 37.7 | 39.4 |
| wt. of total water(g)[a] | 0.22 | 0.75 | 1.86 | 2.70 |
| wt. of free water(g)[a] | 0 | 0.28 | 0.78 | 1.24 |
| wt. of bound water(g)[a] | 0.22 | 0.47 | 1.08 | 1.46 |

(a) ; weight per 1g dry copolymer

Fig. 10. SEM views of cross-sections of copolymer latex membranes. (A)PANAA 2. (B)PAN-AA 3. (C)PANAA 4

acrylic acid component exists in the surface of particle. Hydrophilic component such as acrylic acid may affect the flexibility and morphology of the membrane.

When the water is imbibed in the copolymer membranes, the carboxyl group of acrylic acid forms the hydrogen bonding with water. Subsequently, water molecules associate together and form the hydrogen bonded water clusters. The formation and dissolution of these clusters is governed by local free energy fluctuation, and it is possible to consist of about 100 molecules per cluster with the maximum size.[21] Then, they play an important role in passing solutes through the membrane. It is supposed that the gap between the particles should be filled with water clusters. The solute permeability remarkably increased with the increase of gap and clearness of particles in the membrane.

## Water Permeabilities of Copolymer Membranes

Table 5 shows the water permeabilities of graft copolymer membranes at 38℃. It is revealed that the water permeabilities of copolymer membrenes

Table 5. Water Permeabilities of Copoly(acrylonitrile-acrylic acid) Membranes

| membrane | water permeability $K(cm^2) \times 10^{14}$ |
|---|---|
| PANAA-1 | 0.33 |
| PANAA-2 | 0.76 |
| PANAA-3 | 1.25 |
| PANAA-4 | 27.38 |


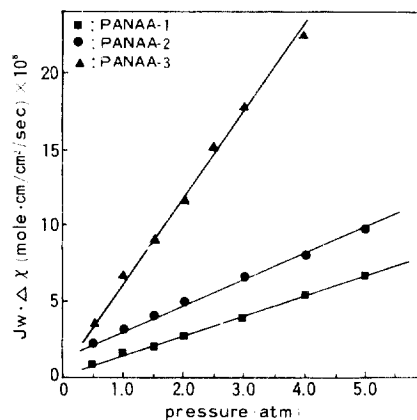
Fig. 11. Dependence of the water flux on applied pressure at 38℃ in copoly(acrylonitrile acrylic acid) membranes.

are larger than that of Cuprophane PT–150 membrane($0.74 \times 10^{15} cm^2$).[8] In the case of PANAA–4 membrane, water permeability is increased abruptly in comparison with other membranes. It is also coincide with the result of solute permeation in the case of large water content.

The water fluxes, $Jw \cdot \Delta x$ of copolymer membranes were also measured in the pressure range of $0.5 \sim 5$ atm. And the dependence of water flux on the applied pressure is shown in Fig. 11. Water flux increased linearly with the applied pressure and therfore, it was revealed that the compaction was not occured in the pressure range of $0.5 \sim 5$ atm.

# REFERENCES

1. S. K. Brauman and B. K. Fritzinger, *J. Appl. Polym. Sci.*, **16**, 2439(1972).

2. Y. Mori, S. Nagaoka, H. Tanzawa, and T. Kikuchi, *J. Biom. Mat. Res.*, **16**, 17(1982).

3. S. Yamashita, S. Nagata, and K. Takakura, *Kobunshi Ronbunshu*, **36**, 257(1979).

4. Y. Ohtsuka, H. Kawaguchi, and Y. Sugi, *J. Appl. Polym. Sci.*, **26**, 1637(1981).

5. K. Sakota and T. Okaya, *J. Appl. Polym. Sci.*, **20**, 1725(1976).

6. A. R. Goodall, M. C. Wilkinson, and J. Hearn, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 2193(1977).

7. H. Kawaguchi, Y. Sugi, and Y. Ohtsuka, *J. Appl. Polym. Sci.*, **26**, 1649(1981).

8. S. Yamanshita, K. Takakura, Y. Imai, and E. Masuhara, *Kobunshi Ronbunshu*, **35**, 283(1978).

9. Y. Ohtsuka, Y. Hirabayashi, and S. Takayama, *Kobunshi Ronbunshu*, **37**, 507(1980).

10. T. A. Jadwin, A. S. Hoffman, and W. R. Vieth, *J. Appl. Polym. Sci.*, **14**, 1339(1970).

11. S. C. Yoon and M. S. Jhon, *J. Appl. Polym. Sci.*, **27**, 4661(1982).

12. H. Yasuda, C. E. Lamaze, and A. Peterlin, *J. Polym. Sci., A-2*, **9**, 1117(1971).

13. J. Kopecet, J. Vacik, and D. Lim, *J. Polym. Sci., A-1*, **9**, 2801(1971).

14. L. Dabrovska and R. Praus, *J. Biom, Mat. Res.*, **12**, 591(1978).

15. J. H. Kim and K. Y. Kim, *Polymer(Korea)*, **10**, 255(1986).

16. Y. Ikada, "Polymers in Medicine", Advances in Polymer Science, **57**, (1984).

17. Y. K. Sung, D. E. Gregonis, M. S. Jhon, and J. D. Andrade, *J. Appl. Polym. Sci.*, **26**, 3719(1981).

18. M. A. Frommer and D. Lancet, *J. Appl. Polym. Sci.*, **16**, 1295(1972).

19. D. G. Pedley and B. J. Tighe, *Brit. Polym. J.*, **11**, 130(1979).

20. W. A. P. Luck, D. Schiöberg and U. Siemann, *J. C. S. Faraday II*, **70**, 136(1980).

21. R. E. Kesting, "Synthetic Polymeric Membranes", McGraw Hill (1971).

22. Y. Ohtsuka and M. Fujii, *Kobunshi Kagaku*, **25**, 375(1968).

23. Y. Ohtsuka, Y. Hirabayashi, and S. Takayama, *Kobunshi Ronbunshu*, **37**, 449(1980).