

Properties of Modified Polyacrylonitrile Membranes Prepared by Copolymerization with Hydrophilic Monomers for Water–Ethanol Mixture Separation

Wen-Yen Chiang, Yi-Haw Lin

Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, 3rd Section, Taipei 10451, Taiwan, Republic of China

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ABSTRACT: A new kind of terpolymer membrane was employed to separate a permselective water–alcohol mixture. This membrane was prepared via the copolymerization of acrylonitrile, sodium salt styrene sulfonic acid (SStSA), and hydroxyethyl methacrylate in dimethylsulfoxide with azobisisobutyronitrile as an initiator. The reaction mechanism, resultant structure, and polymer composition were confirmed by IR and elemental analysis. The effects of the feed composition on the polymer composition, mechanical properties, thermal properties, and degree of swelling were investigated. It was found that water permeated through the membrane preferentially in a water/alcohol system. The

flux increased with the increase of SStSA, but the separation factor decreased drastically with higher SStSA. For a 50 wt % water–ethanol mixture, a flux of 0.65 kg/m² h and a separation factor of 212 were obtained at 30°C when the membrane containing the highest SStSA content was used. The capacities of the metal ions absorbed by the membranes were investigated in the study. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 244–250, 2003

Key words: copolymerization; membranes; separation techniques

INTRODUCTION

The pervaporation process, which is a useful membrane separation technology for a wide variety of organic liquid mixtures, was developed in the mid-1950s. It is a useful process, particularly for separation of close-boiling mixtures, azeotropic mixtures, and others. This separation technique has not yet been put to practical use because of delays in the development of a membrane with high selectivity, including durability during the operation. However, the advantages of its simplicity, low cost, and safety have shown it to be a promising separation process in the near future.

An important aim of membrane research is the discovery and evaluation of a membrane that possesses both high selectivity and high permeation flux while also remaining chemically and mechanically stable after extended contact with the penetrants under the operation conditions of the unit. From this point of view, a series poly(vinyl alcohol) (PVA) and polyacrylonitrile (PAN) membranes were modified in our laboratory. Earlier studies used grafted terpolymers of PVA with poly(maleic anhydride-*co*-methyl methacrylate),¹ *N*-substituted poly(maleimide-*co*-methyl methacrylate),² and PAN.^{3,4} Later, in order to obtain a hydrophilic and hydrophobic

balance, styrene-maleic anhydride copolymers⁵ and styrene-maleic anhydride hydrazine copolymers⁶ were reported as crosslinking agents for PVA. Recently, we succeeded in modifying PVA membranes prepared by the grafting of poly(sodium salt styrene sulfonic acid-*co*-maleic acid) (PSSStSA-*co*-maleic acid).⁷ In this study, we turn hydrophilic matrix PVA into hydrophobic matrix PAN. The modified membranes were expected to possess high water selectivity and acceptable flux, and comparisons of the separation properties in our research series were also conducted.

Although PAN has good film-forming properties and strong mechanical properties, it is not suitable for use as a separation membrane because of its hydrophobic characteristics. In order to improve the above limitation, copolymerizations of AN monomer and other hydrophilic monomers have been performed by many researchers. The results achieved show a high affinity to water. From this viewpoint, SStSA has been considered as an effective monomer because of its high selectivity toward water. The aim of this study is to investigate membranes with high selectivity, acceptable flux for separating water–alcohol systems through pervaporation, and additional functions such as chelation with metal ions.

EXPERIMENTAL

Materials

The AN in the study was purchased from Acros Co. It was freed from its inhibitor by washing with 5% so-

Correspondence to: W.-Y. Chiang (chiang@ttu.edu.tw).

dium hydroxide solution and then with distilled water to remove all alkali traces. It was kept over fused CaCO_3 overnight and distilled before use. Hydroxyethyl methacrylate (HEMA) was purchased from Wako Pure Chemical Industries (Osaka, Japan). It was distilled under reduced pressure. SStSA and azobisisobutyronitrile (AIBN) were purchased from Aldrich Co. (Milwaukee, WI). The AIBN was recrystallized from methanol and dried under a vacuum. Dimethylsulfoxide (DMSO) and dimethylformamide (DMF) were purchased from TEDIA Co. (Fairfield, OH).

Synthesis of PAN/SStSA/HEMA (PANSSHEMA)

Copolymerization of AN, SStSA, and HEMA with different monomer compositions was carried out in a four-necked flask equipped with a stirrer, thermometer, condenser, and dropping funnel. After 3.86 g (0.019 mol) of SStSA was dissolved in 30 mL of DMSO, 24.51 g (0.462 mol) of AN was added. When a homogeneous solution formed, 0.14 g of AIBN was added as an initiator. The monomer with higher reactivity (HEMA) was added dropwise from a dropping funnel, and the reaction was allowed to proceed for 24 h at 65°C. After polymerization the emulsion was precipitated and washed repeatedly with a large amount of MeOH and unreacted AN, SStSA, and HEMA were dissolved in MeOH. The purified polymer was dried in a vacuum oven at 30°C, and PANSSHEMA was obtained.

Viscosity measurement

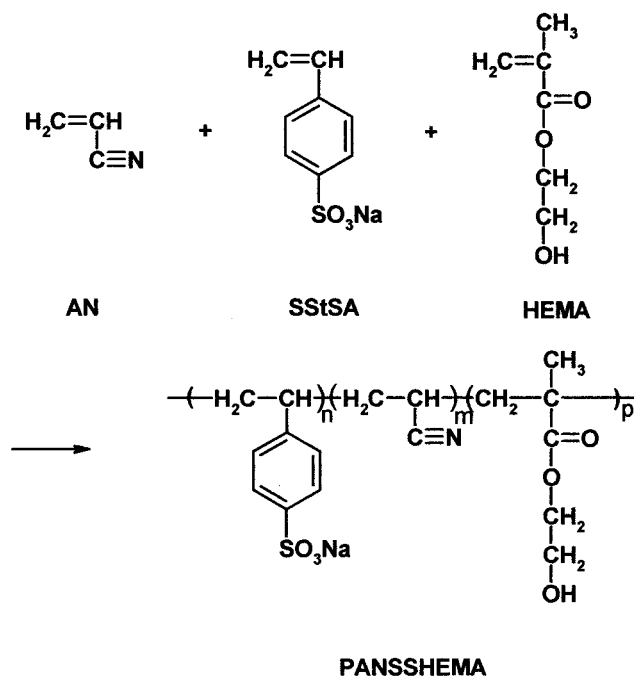
An Ubbelohde viscometer was used for measuring the intrinsic viscosity of the PANSSHEMA. The copolymer solutions were prepared by dissolving the polymers in DMF, and the measurement temperature was adjusted to 30°C. Because the viscosity of the copolymer showed polyelectrolyte characteristics, the intrinsic viscosity was calculated using the Fuoss equation.⁸

Membrane preparation

Membranes were prepared by casting the polymer from a DMF solution with an applicator on a clean smooth glass plate and drying at 40°C for 48 h. The membrane thickness was about 115–120 μm .

Measurements

The measurement of various properties, such as the IR spectra, mechanical properties, thermal properties, and degree of membrane swelling, was made by the method described in earlier work.^{7,9}



Scheme 1 The reaction mechanism of AN, St- SO_3Na , and HEMA.

Pervaporation experiment

The apparatus and procedure for the pervaporation process were essentially the same as described in a previous report.⁸

Soaking method

PANSSHEMA-1 membranes were cut into 1–3 cm test samples at room temperature and soaked individually for 2 days in 25 mL of deionized water containing 0.5 g of metal salts. The adsorptive capacity of the metal ions was determined with a GBC 902 apparatus and evaluated using the difference between the initial and final solution concentrations.

RESULTS AND DISCUSSION

Synthesis of PANSSHEMA

The polymerization reaction mechanism is shown in Scheme 1. The major difficulty encountered in the synthesis of PANSSHEMA was gel formation due to the high reactivity of the monomers, which was prevented using an appropriate solvent and dropping funnel. The FTIR of the PANSSHEMA is given in Figure 1. The figure shows that the characteristic bands appearing at 1200, 1730, and 2240 cm^{-1} correspond to the $\text{S}=\text{O}$ of SStSA, $\text{C}=\text{O}$ of HEMA, and $\text{C}-\text{N}$ of AN. After repeatedly washing the polymer with methanol at high temperature, the unreacted monomers were dissolved in the methanol. According to the IR results, the characteristic bands appeared,

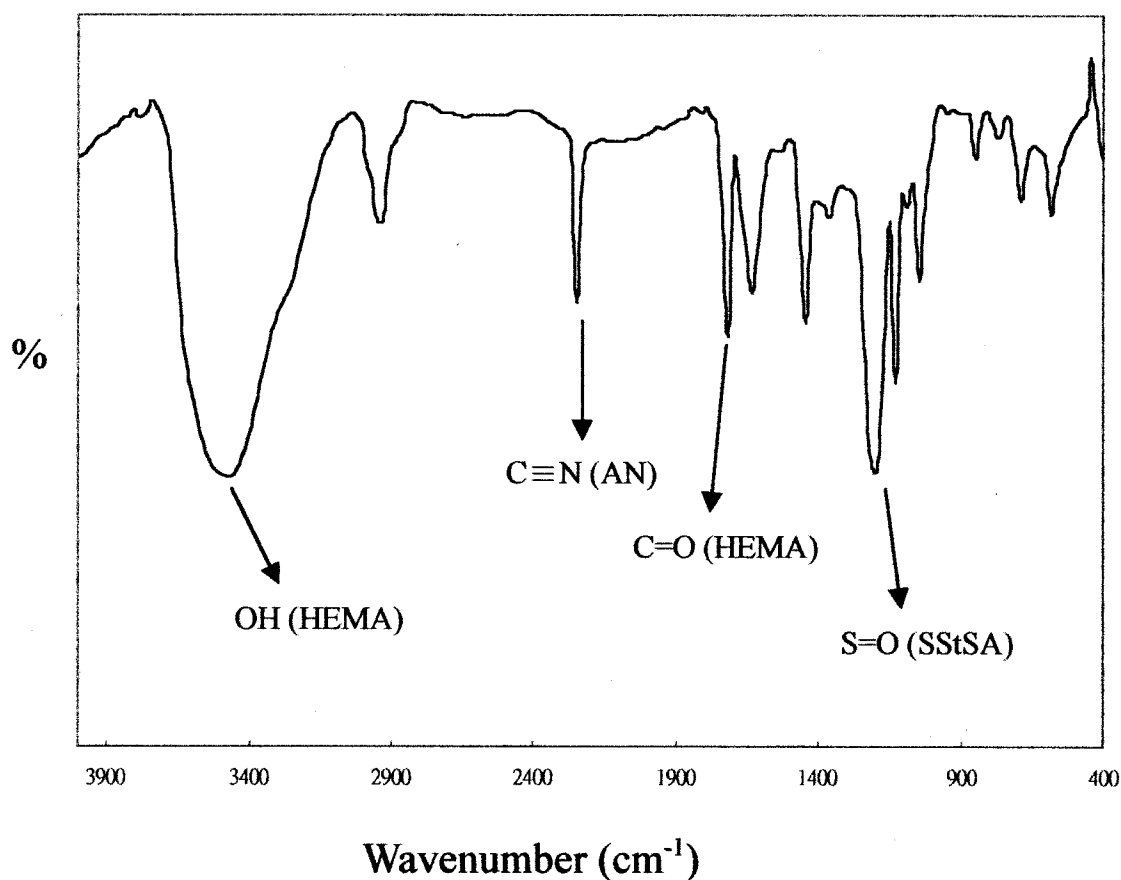


Figure 1 The IR spectra of PANSSHEMA.

thus confirming the copolymerization of AN, SStSA, and HEMA.

The intrinsic viscosities of the polymers were measured using an Ubbelohde viscometer. The relationship between the viscosity and the polymer concentration

(η_{sp}/C) is shown in Figure 2. The η_{sp}/C value increased with the dilution of the polymer concentration, revealing the characteristic properties of polyelectrolytes, which are caused by the $\text{SO}_3^- \text{Na}^+$ group

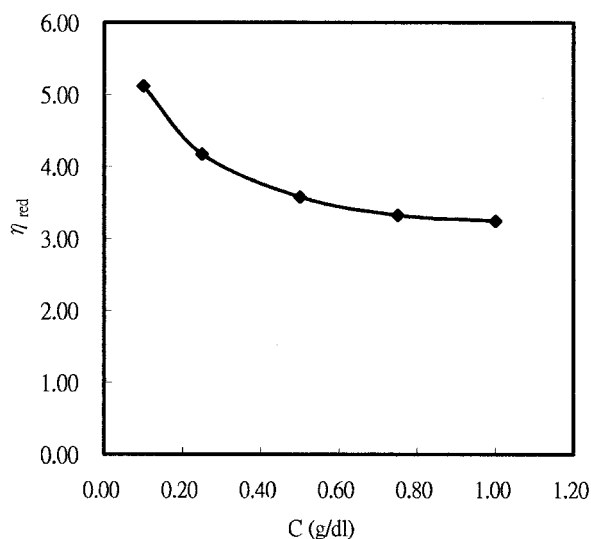


Figure 2 The effect of the concentration on the reduced viscosity of PANSSHEMA-1.

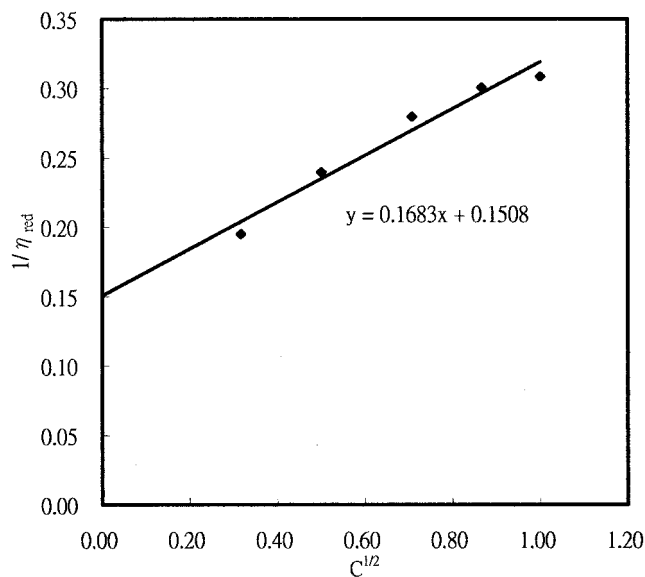


Figure 3 The intrinsic viscosity of PANSSHEMA-1 fitted with the Fuoss equation.

TABLE I
Synthesis of PANSSHEMA

Polymer	Feed Composition (Mole Fraction)			Yield (%)	[η] ^a (DL g ⁻¹)
	AN	SStSA	HEMA		
PANSSHEMA-1 (90/5/5)	90	5	5	44.2	6.63
PANSSHEMA-2 (92.5/3.75/3.75)	92.5	3.75	3.75	44.5	5.23
PANSSHEMA-3 (95/2.5/2.5)	95	2.5	2.5	45.2	4.38

^a Measured in DMF at 30°C; [η], intrinsic viscosity.

of SStSA. The intrinsic viscosity of the polymer is shown in Figure 3 using the Fuoss equation. The relationship between the feed composition and intrinsic viscosity is shown in Table I. Polyelectrolytes normally exhibit properties in solution that are quite different from general polymers when they are ionized in aqueous solutions. The mutual repulsion of their charges causes the chain to expand. PANSSHEMA-1 showed the highest intrinsic viscosity (6.63 dL/g) compared to PANSSHEMA-2 and PANSSHEMA-3. This was due to a greater polyelectrolyte effect being caused by SStSA. The decrease in the SStSA feed composition lowered the chain expansion, which caused the decrease in the intrinsic viscosity. The effect of the SStSA mole fraction in the feed composition played an important role in this study. If the SStSA feed is over 5%, the polymer forms a water-soluble membrane. This phenomenon is caused by the strong SStSA and HEMA hydrophilic characteristics. Moreover, PANSSHEMA-1, PANSSHEMA-2, and PANSSHEMA-3 became water insoluble at lower SStSA and HEMA concentrations. The polymer yields were about 44.5%, because of the higher hydrophilic and smaller polymer molecules dissolved in the methanol. The percentages of N and S in the polymer are given in Table II. The comonomer compositions in the polymer were calculated from the percentages of N and S in the polymer. The SStSA mole fraction increased in the polymer composition with the increase in the SStSA

mole fraction in the feed composition. The AN and HEMA mole fractions were irregularly expressed in the polymer composition with the increase in the AN and HEMA mole fractions in the feed composition. The phenomenon was attributable to the fact that the experimental method was not easy to control precisely. The SStSA mole fraction was higher than the HEMA mole fraction because HEMA is added drop by drop when AN and SStSA copolymerization begins. This experimental method reduced the opportunity for copolymerization between HEMA and AN; moreover, gel formation was prevented.

Mechanical strength

The effect of the polymer composition on the mechanical properties of the PANSSHEMA membranes is shown in Figure 4. For a good membrane, there should be an optimum balance between the tensile strength and elongation at break. PAN-co-SStSA is not suited for the pervaporation process because of its mechanical properties. On incorporation of the polar monomer HEMA, because of the increase in chain flexibility, the tensile strength decreases while the elongation at break increases. The tensile strength increased and the elongation at break decreased with the increase in AN mole fraction. The mole fractions of AN in PANSSHEMA-2 and PANSSHEMA-3 are similar; thus, the mechanical properties of PANSSHEMA

TABLE II
Composition of Polymer

Polymer	N ^a (%)	S ^a (%)	Polymer Composition (Mole Fraction) ^b		
			AN	SStSA	HEMA
PANSSHEMA-1 (90/5/5)	17.56	3.48	86.6	7.5	5.9
PANSSHEMA-2 (92.5/3.75/3.75)	20.58	2.75	92.5	5.4	2.1
PANSSHEMA-3 (95/2.5/2.5)	20.72	1.80	91.8	3.5	4.7

^a Found by elemental analysis.

^b Calculated by the following equations:

$$N\% = \frac{M_{W_{AN}} \times N\%_{AN} \times X\%}{M_{W_{AN}} \times X\% + M_{W_{SStSA}} \times Y\% + M_{W_{HEMA}} \times (1 - X\% - Y\%)}$$

$$S\% = \frac{M_{W_{SStSA}} \times S\%_{SStSA} \times Y\%}{M_{W_{AN}} \times X\% + M_{W_{SStSA}} \times Y\% + M_{W_{HEMA}} \times (1 - X\% - Y\%)}$$

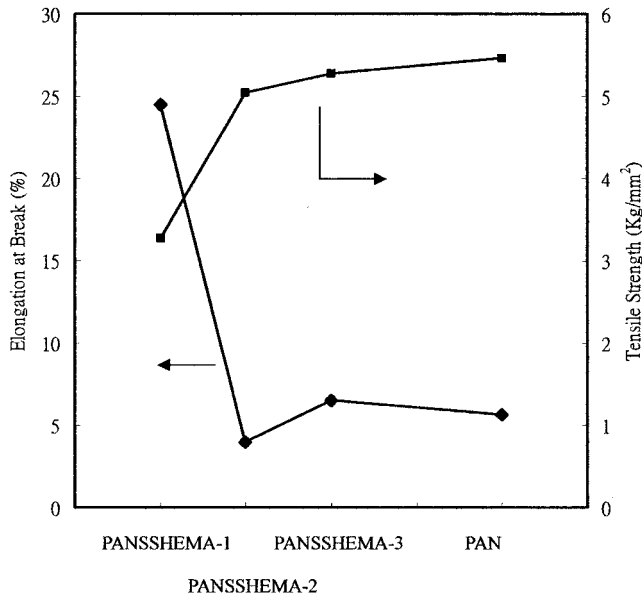


Figure 4 The effect of the composition of PANSSHEMA on the tensile strength and elongation at break of membranes.

SHEMA-2 and PANSSHEMA-3 are also similar. However, the elongation at break of PANSSHEMA-2 was the lowest; it was caused by the mole fraction of HEMA in PANSSHEMA-2. Compared to the PVA series, PANSSHEMA is not as firm as the PVA series. Because of insufficient mechanical strength, the AN series is limited to pervaporation.

TABLE III
Swelling Degree of PANSSHEMA for Each Pure Component at 30°C

Polymer	Water (wt %)	Methanol (wt %)	Ethanol (wt %)	Isopropanol (wt %)
PANSSHEMA-1	50.9	18.8	9.7	7.3
PANSSHEMA-2	43.3	14.4	3.8	3.7
PANSSHEMA-3	20.5	11.3	3	2.8

Thermal property

A TGA thermogram is shown in Figure 5. The threshold degradation temperature of 352°C is sufficiently above the temperature at which a pervaporation experiment is expected to be carried out. According to the DSC results in the literature, the CN of AN will form a ring at 269°C. Thus, the higher residual weights of PANSSHEMA-2 than PANSSHEMA-1 and PANSSHEMA-3 could be due to the AN ring formation and the lower HEMA thermal resistance. A 55.25% residue was caused by high AN content and low HEMA content in PANSSHEMA-2.

Degree of membrane swelling

Table III shows the effect of the polymer composition on the degree of membrane swelling in pure water, methanol, ethanol, and isopropanol. Water causes membrane swelling to a far greater degree than alcohol because of the strength of the hydrogen-bonding

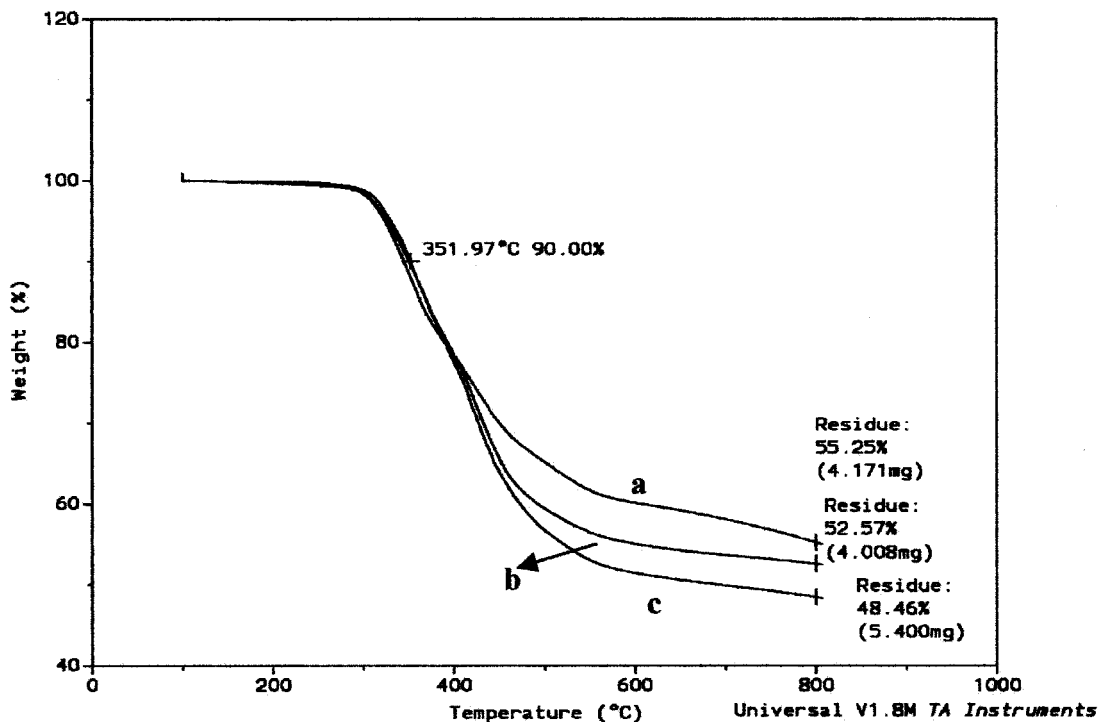


Figure 5 TGA thermograms of PANSSHEMA-2 (curve a), PANSSHEMA-3 (curve b), and PANSSHEMA-1 (curve c).

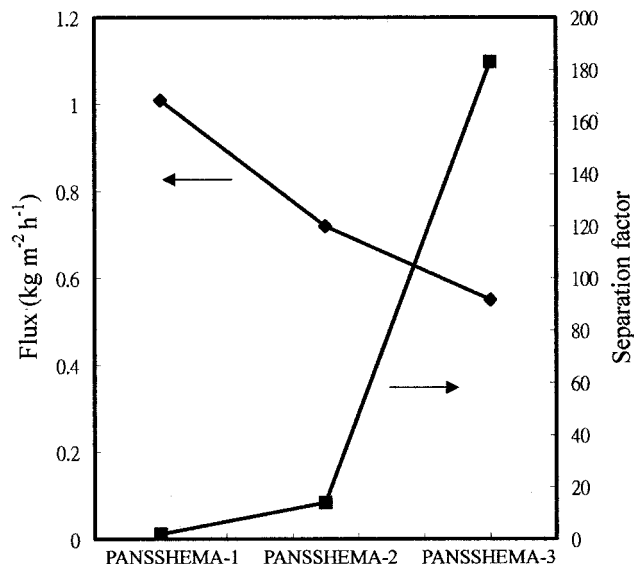


Figure 6 The permeability and separation factors of PANSSHEMA for 1:1 (w/w) water/methanol mixtures.

interaction. Moreover, an increase in the SStSA and HEMA concentration is an increase in hydrophilic groups, leading to an increase in the degree of membrane swelling. Similar series have been reported in the literature¹⁰ in which PAN-based phosphoric acid containing membranes were discussed. The swelling degree toward water in membranes containing 3.6 mol % monoacryloxyethyl phosphate was 16%. In our case, the degree of swelling toward water in PANSSHEMA was in the range of 20.5–50.9%, which reveals a better affinity to water. It should be noted that the membranes in a methanol system have a greater degree of membrane swelling than membranes in an ethanol system, and the membranes in an ethanol system have a greater degree of membrane swelling than membranes in an isopropanol system. In general, as the carbon number in alcohol increases, the hydro-

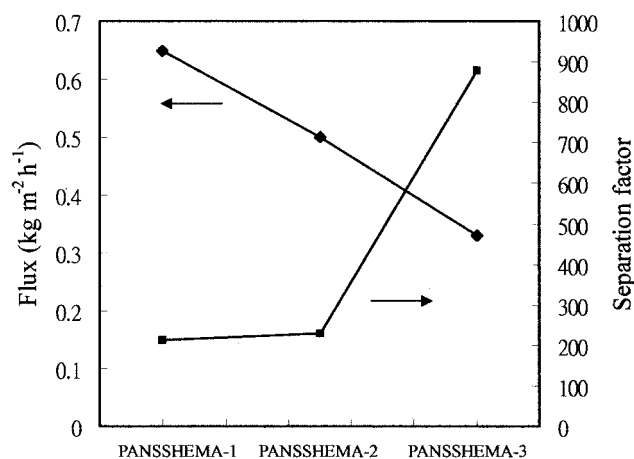


Figure 7 The permeability and separation factors of PANSSHEMA for 1:1 (w/w) water/methanol mixtures.

TABLE IV
Amount of Metal Ions Absorbed by PANSSHEMA-1 in Metal Chloride Aqueous Solution

	Cu ²⁺	Ni ²⁺	Co ²⁺
Concentration (ppm)			
Initial	7455	4954	4954
Final	5480	4192	4354
Adsorptive ratio (%)	26.5	15.4	12.1
Adsorptive capacity (mmol/g)	20	8.2	6.4

philic ability decreases. The difference in the strength of the hydrogen-bonding interaction between membrane–water and membrane–alcohol systems may lead to a selective separation by the membrane.

Water/alcohol pervaporation

Base on the degree of membrane swelling, a membrane with higher sulfuric acid group content shows a higher affinity to water and alcohol. Therefore, the flux is increased by increasing the SStSA content in the membranes, as shown in Figure 6. The SStSA content in PANSSHEMA-1 was the highest, so a flux of 1.01 kg/m² h was obtained while the 50 wt % water and methanol mixture were separated. The degree of membrane swelling to water was greater than that to alcohol, and it shows a higher selectivity to water for a water–alcohol mixture. Note from Figure 6 that the separation factor increased with a decrease in the membrane SStSA content and it increased substantially as PANSSHEMA-3 was used. The separation factor of 183 that was obtained was due to the higher AN content and lower SStSA content in PANSSHEMA-3.

From the membrane swelling, a membrane can have a stronger affinity to methanol than to ethanol. In this case, the flux of the membrane for a water–methanol mixture was greater than for a water–ethanol mixture, as shown in Figure 7. The affinity and size of the alcohol molecules caused this result. The flux trend and the separation factor in the water/ethanol system were identical to the water/methanol system. A separation factor of 212 was obtained when PANSSHEMA-1 was used for the separation of a 50 wt % water and ethanol mixture. This result was greater than the separation factor of 2 obtained when PANSSHEMA-1 was used to separate a 50 wt % water and methanol mixture. Improvements in the separation factor and acceptable flux indicate that PANSSHEMA-1 and PANSSHEMA-2 were suited to separate a water and ethanol mixture. Compared with the PVA series, the PAN series possessed a higher separation factor and lower flux. The PANSSHEMA series improved the separation factor of PVA-*g*-St-SO₃Na-*co*-maleic acid⁷ in a water/ethanol system and still kept an acceptable flux.

TABLE V
Comparison of Permsepation Results of AN Series with Other Reports

Membrane	Ethanol (wt %)	Tem (°C)	α	Flux (kg m ⁻² h ⁻¹)	$\alpha \times$ Flux	Thickness (μ m)	Ref.
PANSSHEMA-1 ^a	50	30	212	0.65	137.8	120	—
PANSSHEMA-2 ^a	50	30	230	0.5	115	120	—
PANSSHEMA-3 ^a	50	30	879	0.33	290.1	120	—
PAN-EA ^a	50	30	75	0.03	6.4	100	2
Modified PVA-g-AN ^a	50	30	4	0.7	2.8	100	4
Poly(4-vinyl pyridine-co-AN)	50	30	10	0.02	0.2	25	11
PAN/CA	—	60	420	0.05	21	33	12
Poly(AA-co-AN)	50	30	50	0.03	1.5	15	13
3-(<i>N,N</i> -Dimethyl)amino-propyl acrylamide-co-AN	50	30	528	0.01	5.28	15	14
1-Butyl-4-vinyl pyridium iodide-co-AN	50	15	50	0.04	2	25	15
PAN/CS	90	60	8000	0.26	2080	—	16

^a The membranes were synthesized by our laboratory.
 α , separation factor.

Adsorptive capacity for various metal ions

When the film was immersed in the aqueous solution containing metal ions, the film expanded because of water absorption by the hydrophilic groups. The —CN and —OH in PANSSHEMA-1 chelate with metal ions. Table IV shows the adsorptive ratio and adsorptive capacities of PANSSHEMA-1 for different metal ions under the same conditions. The PANSSHEMA-1 expresses good effects from chelation with Co²⁺, Ni²⁺, and Cu²⁺, especially to Cu²⁺ with larger molecular bonds.

CONCLUSIONS

We improved the hydrophilic ability of PAN by copolymerization with SStSA and HEMA. Moreover, this copolymer composition was insoluble in water but possessed the highest hydrophilic ability. Compared with PAN and the PAN series as shown in Table V, the flux of the PANSSHEMA series rose considerably and exhibited a superior separation factor when PANSSHEMA-3 was used for separation of water/methanol or water/ethanol mixtures. Although PANSSHEMA-3 possessed good selectivity, the flux was too low. Hence, PANSSHEMA-2 was more suited than PANSSHEMA-3 for separation of water/ethanol mixtures. The membrane expanded because of the water absorption by the hydrophilic groups. The ideal chelate condition was caused by appropriate hydrophilic groups

(—SO₃Na) and sufficient chelate groups (—CN and —OH). A good adsorptive capacity of PANSSHEMA-1 for Cu²⁺ metal ions was obtained under the same conditions. This expresses another function of the PANSSHEMA series.

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