Separation of Water-Ethanol Mixture by Pervaporation through Hydrolyzed Polyacrylonitrile Hollow Fiber Membranes

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ABSTRACT: For the purpose of separating water-ethanol mixtures by the use of the pervaporation technique, new composite membranes composed of polyion complexes (PIC) as a separating layer were developed. The polyion complex structure, consisting of polyacrylic acid (PAA) and polycation, provided excellent permeation rate and selectivity. To obtain a composite hollow fiber membrane, a new technique was developed instead of coating. That is, the polyacrylonitrile membrane was partially hydrolyzed to introduce a carboxylic group, and then converted to a polyion complex. The alkaline hydrolysis reaction and the formation of the separating layer were analyzed by the use of IR, SEM, and EDX. In this manner, modules with effective membrane area up to 6m² have been prepared.

KEY WORDS Polyacrylic Acid / Polyacrylonitrile / Ethanol / Water / Pervaporation / Polyion Complex / Membrane / Ionene/

Pervaporation (PV) separation of organic mixtures is a rather new membrane technology compared with reverse osmosis and ultrafiltration etc. from the viewpoint of practical application. However, since GFT first established the commercial base pervaporator in Brazil by the use of a crosslinked PVA composite membrane, a lot of membrane materials have been examined to improve membrane performance and to investigate the transport mechanism.¹ Especially, many works regarding the dehydration of azeotropic ethanol have been reported. In Japan, research on high performance ethanol dehydration membranes has been conducted under two national R&D projects "Synthetic Membranes for New Separation Technology" and "Membrane Technology for Alcohol Purification", sponsored by the Ministry of International Trade and Industry (MITI).

In this paper, the PV separation characteristics of polyacrylic acid ion complex membranes which are developed under these projects will be reported.

EXPERIMENTAL

Materials

Polyacrylic acid (PAA) was obtained either by the usual radical polymerization or by being purchased from Scientific Polymer Products Inc. Microporous polyethersulfone (PES) and Polyacrylonitrile (PAN) membranes were supplied by Daicel Chemical

Industries, Ltd. Ionene type polycations were synthesized through the Menshutkin reactions.²

Membrane Preparation

Two types of membrane preparation were examined to obtain a composite membrane, i.e. coating and PAN hydrolysis techniques.

- Coating Method -

PAA aqueous solutions were cast onto the supporting membranes with a wire-bar applicator (0.15mm wire diameter). Coated membranes were dried under the clean air at 20 °C for 30 minutes. In the case of crosslinked PAA membranes, crosslinking agents such as ethyleneglycol-diglycidylether were added to the PAA solution prior to coating and crosslinking was allowed to proceed at 100°C for 10minutes in a clean oven. In order to convert the PAA to polyion complexes (PIC), these membranes were dipped in a 2 wt% aqueous solution of polycations at room temperature for 12 hrs.

- PAN Hydrolysis Method -

The PAN membrane was partially hydrolyzed by immersing it into NaOH aqueous solution to convert a nitrile group into a carboxyl group at 80°C. After excess alkali was removed with enough water, then the membrane was immersed into the polycation solution to form PIC.

Pervaporation performance was measured by using cells for flat membranes or by using hollow fiber modules having various surface areas up to 6m². Details about the apparatus and procedures were reported in a previous paper.^{3,4}

RESULTS AND DISCUSSION

Flat Membranes

In this study, we focused on polyacrylic acid (PAA) as a membrane material. PAA is considered to be suitable as a water selective membrane material from several points. As shown in Table I, PAA has a high charge density based on the dissociated carboxyl group. However, when the feed solution to be separated has a low concentration of ethanol, PAA is dissolved or significantly swollen expecting a remarkable decline of selectivity.

Resistance to a wide range of feed composition can be achieved by converting PAA into a three dimensional structure by crosslinking. The carboxyl group of PAA can be used as a crosslinking site. Finally, the high molecular weight polymer, which is effective for making thin and tough membranes, can be easily synthesized by the usual radical polymerization.

Table I. Features of polyacrylic acid as a membrane material

1 Polyelectrolyte - High charge density	
$\left(\begin{array}{c} \text{CH}_2-\text{CH} \\ \\ \text{COOH} \end{array} \right)_n$	$\xrightarrow{\text{Salt form}} \left(\begin{array}{c} \text{CH}_2-\text{CH} \\ \\ \text{COOM} \end{array} \right)_n \quad \text{M:Alkali metal}$
2 Crosslinkable through carboxyl group	----- Epoxy, Isocyanate compounds
3 High molecular weight polymer	----- Radical polymerization Plasma polymerization

Table II. Classification of polyacrylic acid based PV membranes

Type	Material	Support or trunk polymer	Reference
Homopolymer	PAA coated onto various substrates	Polysulfone Polyethersulfone	5-7
Copolymer	PAA/PAN		8,9
Blend	CMC/PAA(Na), Nylon-6/PAA Nylon-66/PAA		10-12
Graft	Electron beam irradiation Plasma initiation Gamma-ray irradiation Chemical method	PE, PAN, PVF ₂ , Porous PP, etc. PVA, PAA/Nylon-6 PVA	13-25
Polyion complex	PAA/Polycation (Composite membrane)	PES, PAN	this study

As shown in Table II, a lot of research using PAA as a membrane component has been reported recently.⁵⁻²⁵

As reported earlier,⁵ the PAA composite membrane showed excellent separation properties, when PAA was converted into an alkali salt form. However, it was found that the high separation declines remarkably with PV operation. Figure 1 shows the typical features of PAA-potassium salt composite membranes crosslinked with diamine and diepoxide. This lack of long term stability was also observed for the PAA grafted PAN membranes¹⁵ and was a serious problem for the practical uses.

Figure 1. Separation Properties of PAA/K-salt membranes as a function of time.
PAA: Mw 500,000 crosslinked
PV: 95wt% EtOH at 70°C

Figure 2. Separation properties of PIC membranes as a function of time
PAA: Mw 500,000 crosslinked with diepoxide

From the fact that the separation properties were restored by reneutralizing the membrane with alkaline and through quantitative analysis of the alkaline ion in the membrane, it was found that the decrease of the separation properties was caused by the elution of the alkaline metal cations out of the membrane. Instead of the alkali, multivalent cations such as Ca^{2+} and Al^{3+} were examined for keeping the dissociation through ionic crosslinking. However, the PAA membranes substituting multivalent counterions mostly yielded a relatively low permeation rate and low selectivity accompanying membrane brittleness.

Next, several kinds of polycations were examined for the purpose of stabilizing the PAA dissociation due to the high order of interaction between oppositely charged polymers. Polyion complexes (PIC) can be easily formed by simply immersing the PAA composite membrane into the appropriate concentration and PH of the polycation solution. Figure 2 shows the separation properties of the PIC membranes in which the counter polycations are polyethyleneimine and PCA-107, respectively. From a comparison of Fig.2 with Fig.1, it is clear that PIC formation is quite effective for maintaining the separation properties of PAA membranes.

To elucidate the effect of the polycation on the separation properties, various weak and strong polycations were examined. From these measurements, it was found that so called "lonenes", gave membranes of much higher separation properties compared with weak polycations such as polyethyleneimine and polyallylamine (Table III). It is still not clear why the PAA complexes with ionenes yield the better properties. Kurokawa *et al.* measured the sorption isotherms of water and some organic solvents for various PICs.²⁶ They observed that PIC consisting of polystyrenesulfonate (PSS-Na) and an ionene shows the lesser sorptivity for organic solvents such as methanol. Thus, it may be considered that the present systems (PAA/ionene) also have similar sorption characteristics (solubility selectivity dominant) and reject ethanol more completely out of the membrane.

In the case of PIC consisting of a weak polyanion, it has been known that PH in the mixing solution affects the composition.²⁷ The molar ratio (PCA)/(PAA) increased with increasing PH and approached unity at high PH regions.

Table III. Separation of PAA polyion complex membranes

Counter Cation	Permeation rate Q (kg/m ² ·hr)	Water in permeate (wt%)	Separation factor $\alpha(\text{H}_2\text{O}/\text{EtOH})$
Polyethyleneimine	0.83	92.05	220
Polyallylamine	0.51	97.53	750
PCA-101	0.79	98.90	1710
PCA-107	0.82	99.03	1940
PAL-2	0.34	97.76	830
PCQ-1	0.22	95.24	380

PAA: MW 500,000, crosslinked with diepoxide
Evaluation: PV with 95wt% EtOH of 70°C

Figure 3. Effect of PCA/PAA ratio on separation factor. (PAA:MW 4,000,000, uncrosslinked)

Figure 4. Effect of PCA/PAA ratio on permeation rate. (PAA:MW 4,000,000, uncrosslinked)

The effects of PCA-107/PAA composition on the separation factor and permeation rate are shown in Figures 3 and 4, respectively. Separation properties, especially permeation rate, increase with increasing the amount of associated PCA-107. To clarify this result, the permeation rate, $Q(\text{total})$, is separated into two parts, i.e. $Q(\text{EtOH})$ and $Q(\text{H}_2\text{O})$, in Figure 4. High water selectivity has been attributed not only to the increase of $Q(\text{H}_2\text{O})$, but to the appreciable decrease of $Q(\text{EtOH})$. It seems that the quantitative complexation (1:1 ratio) maximizing the dissociation of PAA plays a dominant role in increasing hydrophilicity and separation property.

Table IV Comparison with other hydrophilic membranes

Material	Ethanol in feed (wt%)	Temp. (°C)	Separation factor $\alpha(\text{H}_2\text{O}/\text{EtOH})$	Permeation rate Q (kg/m ² ·hr)	$Q \times \alpha$	Ref.
Crosslinked PVA	95	80	9,500	0.01	95	28
Poly(hydroxy methylene)	95	60	>8,950	0.013	116	29,30
Chitosan (crosslinked with H ₂ SO ₄)	90	60	6,500	0.1	650	31
Sulfonated polyethylene	Cs ⁺	85.4	725	0.152	110	32
	Na ⁺	85.4	671	0.080	54	32
CMC(DS 0.8, Na ⁺)	90	30	2,430	0.052 ¹⁾	126	10
Alginate acid (crosslinked with Co ²⁺)	90	60	5,000	0.15	750	31
PAA/PCA-107	95	60	3,510	1.63	5720	This study
		70	2,890	2.17	6270	

1) Permeation rate: kg·mil/m²·hr

Through extensive work for optimizing the membrane preparation, membranes having excellent separation properties ($Q = 1.6 \text{ Kg/m}^2\text{hr}$ & $\alpha = 3,500$ for feed mixture of 95wt% EtOH at 60°C) have been developed. In Table IV, the highly water permselective pervaporation membranes are cited from literature, and compared with the data obtained in this study. With regard to the productivity of membranes, the PIC composite membrane has achieved the highest value. Through these comparisons, it has been proved that this PAA-based PIC membrane has a high separation potential for the dehydration of azeotropic mixture of ethanol.

Hollow Fiber Membranes

In a previous section, the PIC flat membranes were prepared successfully by the use of a coating technique. When we joined the national project "Membrane Technology for Alcohol Purification" in 1987, hollow fiber membranes were selected to develop the large-scale pervaporator due to its compactness, ease of scale up, expecting uniform feed flow and so on. In the case of hollow fiber PV operation, two methods can be considered. That is, the feed is supplied to the inside of hollow fiber membrane and other is the outside. We have chosen the former method because the uniform feed flow and minimizing an increase of down stream pressure affecting permeation rate. When taking this separation method, the membrane should have an active separating layer inside. The coating technique is rather difficult to make a uniform and pin-hole free layer on the inside wall for more than thousands of hollow fiber. Instead of coating, PAN hydrolysis method was newly developed to obtain the PIC composite hollow fiber membranes.

It is well known that a highly water-swollen polymer can be obtained by hydrolyzing PAN with alkali or acid.³³⁻³⁵ Reaction scheme of the hydrolysis with alkali is shown in Figure 5.

To confirm that this technique can be applied to membrane preparation, PAN flat membrane (UF Membrane: DUY-M) was initially used for preliminary investigation. From the IR measurement, it was found that new absorption bands related to the ionized carboxyl group appeared after 30 minutes immersion in 1N-NaOH at 80°C .

The separation properties were measured after PIC formation with PCA-107. Figure 6 shows the effect of hydrolysis time on the membrane properties. Permeation rate rapidly decreased with the reaction time after 40 minutes. However, the separation factor had a maximum of around 60 min.

Figure 5. Reaction Scheme of PAN hydrolysis.

Figure 6 Effect of hydrolysis time on pervaporation properties of PIC membrane.
Base membrane: DUY-M, Hydrolysis: 1N-NaOH at 80°C

From these results, it was found that the PAN hydrolysis method can be used for forming the PIC layer at the membrane surface and the high performance membrane can be obtained by controlling the reaction conditions.

To apply this technique to the PAN hollow fiber, various hydrolysis conditions were examined. Here, PAN hollow fiber has a unique structure in which the outer surface of the membrane has macropores ($\sim 1.0 \mu\text{m}$) to reduce the permeation resistance, and the inner surface has micropores (ultrafiltration level).

Figures 7 and 8 show the relationships between the separation properties of PIC membrane and hydrolyzing time in different concentrations and temperatures of NaOH aqueous solution. Some membranes show higher separation factors compared with the DUY-M flat membrane. These figures also show that the separation properties can be controlled by changing the reaction conditions (NaOH concentration, temperature, and reaction time). Low temperature and rather low concentration of NaOH (0.5~1.0N) are preferable because

Figure 7. Effect of hydrolysis time and concentration of NaOH on pervaporation properties
Feed: 95wt% EtOH, 60°C

the slopes of these curves level off.

In order to observe the membrane structure, SEM measurement was done for the samples of before and after hydrolysis. These photographs show that the micropores on the inner surface disappeared after 40 minutes of hydrolysis, and a separating layer of ca. 0.5 μm thick was formed. On the other hand, pores on the outer surface remained at their initial size. These findings indicate that pores of less than 0.1 μm in diameter are covered by forming carboxyl group and heat shrinking.

Furthermore, the hydrolyzed PAN hollow fiber has maintained almost all of initial mechanical properties.

In this manner, 1,000 fibers were treated at a time to prepare a module with effective membrane area of 1m^2 . The durability test was conducted by using this module for 12 days. The result is shown in Figure 9. The module showed the high permeation rates and separation factors of 0.42 $\text{Kg}/\text{m}^2\text{hr}$ and 5,000~6,000 in 95wt% EtOH, and 0.054 $\text{Kg}/\text{m}^2\text{hr}$, 4,000~6,000 in 99wt% EtOH at 60 $^{\circ}\text{C}$.

Recently, a larger module having membrane area of 6m^2 was developed to test in bench plant operation.

CONCLUSION

The alkali salt form of PAA membrane showed higher water selectivity, but the high separation declined with the PV operations due to the elution of counter ions. Instead of alkaline metal, various polycations were used to ionize PAA and to form polyion complexes. PIC structure was quite effective in stabilizing the separation properties. To prepare the PIC hollow fiber, PAN hydrolysis method was newly developed instead of coating. The uniform separating layer was formed by the alkali hydrolysis, and the optimum membrane was obtained by controlling hydrolysis reaction such as temperature and alkali concentration.

Figure 8. Effect of hydrolysis time and temperature on pervaporation properties
Feed: 95wt% EtOH, 60 $^{\circ}\text{C}$

Figure 9 Pervaporation properties of hollow fiber module.
(Effective membrane area = 1m²)

Based on this technique, it became possible to prepare the excellent membrane module which had the following performance, separation factor~ 5,000, permeation rate~ 0.42 Kg/m²hr for 95wt%, 60 °C feed.

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REFERENCES

1. B.D. Gupta and A.K. Mukherjee, *Polym.-Plast. Technol. Eng.*, **29**, 299 (1990)
2. E. Tsuchida, K. Sanada, and I. Shinohara, *Kogyokagaku zasshi*, **74**, 756 (1971)
3. H. Karakane, M. Tsuyumoto, Y. Maeda, K. Satoh and Z. Honda, *Proceedings of Third International Conference on Pervaporation Processes in the Chemical Industry at Nancy*, p.194 (1988)
4. M. Tsuyumoto, H. Karakane, Y. Maeda, and H. Tsugaya, *Proceedings of Fourth International Conference on Pervaporation Processes in the Chemical Industry at Ft. Lauderdale*, p.157 (1989)
5. M. Tsuyumoto, H. Karakane, Y. Maeda, and Z. Honda, *Polymer Preprints, Japan (Eng. Ed.)*, **36**, E728 (1987)
6. Japanese Patent JP63-126506A (1988)
7. British Patent GB 2174619A,
8. M. Yoshikawa, T. Yukoshi, K. Sanui, and N. Ogata, *J. Polym. Sci., Polym. Lett. Ed.*, **22**, 473 (1984)
9. M. Yoshikawa, T. Yukoshi, K. Sanui, and N. Ogata, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 1585 (1985)
10. C.E. Reineke, J.A. Jagodzinski, and K.R. Denslow, *J. Memb. Sci.*, **32**, 207 (1987)
11. Y.F. Xu and R.Y.M. Huang, *J. Appl. Polym. Sci.*, **36**, 1121 (1988)
12. X.P. Zhao and R.Y.M. Huang, *J. Appl. Polym. Sci.*, **41**, 2133 (1988)
13. J. Neel, Q.T. Nguyen, R. Clement, and R. Francois, *Symp. Proc: ICOM'87*, 479 (1987)
14. J. Neel, Q.T. Nguyen, R. Clement, and R. Francois, *Proceedings of Second International Conference on Pervaporation Processes in the Chemical Industry*, p.35 (1987)
15. G. Ellinghorst, A. Niemöller, H. Scholz and H. Steinhauser, *Proceedings of Second International Conference on Pervaporation Processes in the Chemical Industry*, p.79 (1987)
16. A. Niemöller, H. Scholz, B. Götz and G. Ellinghorst, *J. Memb. Sci.*, **36**, 385 (1988)
17. T. Hirotsu, *Kino Zairyo*, **6**, 33 (1986)
18. T. Hirotsu, *Ind. Eng. Chem. Res.*, **26**, 1287 (1987)
19. T. Hirotsu, *J. Appl. Polym. Sci.*, **34**, 1159 (1987)
20. T. Hirotsu and S. Nakajima, *J. Appl. Polym. Sci.*, **36**, 177 (1988)
21. R.Y.M. Huang and Y.F. Xu, *Eur. Polym. J.*, **24**, 927 (1988)
22. V. Shantora and R.Y.M. Huang, *J. Appl. Polym. Sci.*, **26**, 3223 (1981)
23. T. Hirotsu, *Bull. Res. Inst. Polym. Text.*, No.156, 23 (1987)
24. R. François, Q.T. Nguyen, and J. Néel, *Makromol. Chem., Macromol. Symp.*, **23**, 421 (1989)
25. Z.H. Ping, Q.T. Nguyen, R. Clément, and J. Néel, *J. Memb. Sci.*, **48**, 297 (1990)
26. Y. Kurokawa, N. Shirakawa, M. Terada and N. Yui, *J. Appl. Polym. Sci.*, **25**, 1645 (1980)
27. K. Abe, H. Ohno, and E. Tsuchida, *Makromol. Chem.*, **178**, 2285 (1977)
28. Japanese Patent JP59-109204A (1984)
29. M. Nakamura, I. Terada, S. Samejima and M. Nakao, *Polymer Preprints, Japan*, **37**, 503 (1988)
30. I. Terada, M. Nakamura, and M. Nakao, *Desalination*, **70**, 455

- (1988)
31. A. Mochizuki, Y. Sato, H. Ogawara and S. Yamashita, *Polymer Preprints, Japan*, **35**, 2202 (1986)
 32. I. Cabasso, E. Korngold, and Z.Z. Liu, *J. Polym. Sci., Polym. Lett. Ed.*, **23**, 577 (1985)
 33. Pushpa Bajaj, R.B. Chavan, and B. Manjeet, *J. Macromol. Sci.-Chem.*, **A22**, 1219 (1985)
 34. N.S. Batty and J.T. Guthrie, *Polymer*, **19**, 1145 (1978)
 35. N.S. Batty and J.T. Guthrie, *Makromol. Chem.*, **182**, 71 (1978)