

Development of Polyion Complex Membranes for the Separation of Water–Alcohol Mixtures. III. Preparation of Polyion Complex Membranes Based on the k-Carrageenan for the Pervaporation Separation of Water–Ethanol

JONGGEON JEGAL* and KEW-HO LEE

Membrane and Separation Lab., Advanced Polymer Division, Korea Research Institute of Chemical Technology, P.O. Box 9, Daedeog Danji, Taejeon, 305-606, Korea

SYNOPSIS

Pervaporation separation of water–ethanol was carried out with polyion complex membranes based on k-carrageenan. The polyion complex membranes were prepared by the ion complex formation between k-carrageenan (anionic polymer) and poly{1,3-bis[4-alkylpyridinium]propane bromide}s (cationic polymers) with different numbers of methylene units between two ionic sites within a repeating unit, respectively. The ion complex membranes were characterized with FT-IR, X-ray diffractometry. Dehydration of 90 wt % aqueous ethanol solution was carried out at different temperatures (30, 40, 50, and 60°C). The selectivity and permeability through them were very good over a wide temperature range; in the case of the polyion complex membrane consisting of k-carrageenan and poly{1,3-bis[4-ethylpyridinium]propane bromide}, the permselectivity was 45,000 and permeability was 150 g/m² h at 30°C. With increasing operating temperature, the permeability was increased highly but the selectivity decreased slightly. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

For dehydration of alcohol solutions by pervaporation process, it has been well known that hydrophilic membranes are better than hydrophobic membranes. Therefore, many researchers have used many different hydrophilic membrane materials.^{1–10} Among them are poly(vinyl alcohol), poly(acrylic acid), and ionic polymers such as sodium alginate and chitosan.^{6–10} Generally speaking, the membranes made from hydrophilic materials have showed very good permselective properties in the separation of water–ethanol. However, each membrane had some problems. For instance, the poly(vinyl alcohol) membranes showed very good permselectivity but relatively low permeability, and ionic polymer membranes showed very good permselectivity and permeability but relatively low long-time stability.

Knowing these difficulties, many people have tried to create new types of membranes. Polyion complex membranes are some of them.^{6,7} Polyion complex membranes are formed by the ion complex formation between anionic polymer and cationic polymer. The polyion complex membrane has been reported to have very good permselectivity and permeability with good long time stability.⁷ However, the effects of the ion contents and counter ion species of cationic polymers or anionic polymers on the membrane properties such as permselectivity and permeability have been rarely studied so far. On this base, new cationic polymers based on the 1,3-di(4-pyridyl)propane were synthesized in our laboratory.¹¹

In this study, k-carrageenan (anionic polymer) and a series of poly{1,3-bis[4-alkylpyridinium]propane bromide}s with different alkyl groups such as ethyl, butyl, hexyl, and octyl (cationic polymers) were used for the formation of polyion complex membranes. The k-carrageenan, selected in this study as an anionic polymer, is structural polysaccharide of the red seaweed and contains one sulfate

* To whom correspondence should be addressed.

group in each disaccharide repeating unit as shown in Figure 1.

k-Carrageenan was used in this study because its sulfate groups are good anions for the ion complex formation with pyridinium cations of poly{1,3-bis[4-alkylpyridinium]propane bromide}s. The membranes were characterized by using FTIR and X-ray diffractometry. The membrane properties of pervaporation separation of water-ethanol were carried out with a general pervaporation process. The effect of the ion contents of a series of polyion complex membranes on the separation of water-ethanol by pervaporation was studied.

EXPERIMENTAL

Materials

k-Carrageenan (Sigma Co.) and poly{1,3-bis[4-alkylpyridinium]propane bromide}s such as poly{1,3-bis[4-ethylpyridinium]propane bromide}, poly{1,3-bis[4-butylpyridinium]propane bromide}, poly{1,3-bis[4-hexylpyridinium]propane bromide}, and poly{1,3-bis[4-octylpyridinium]propane bromide}, synthesized by quaternization polymerization of 1,3-di(4-pyridyl)propane with respective dibromoalkanes in our laboratory (cationic polymers)¹¹ were used for the preparation of the polyion complex membranes. Distilled water was used for the solvent

of the polymers in the film casting. Ethanol (HPLC grade, Aldrich Co.) was used as solvent.

Membrane Formation

The polyion complex membranes were prepared by dipping k-carrageenan films into the aqueous cationic polymer solutions. Prepared by casting 1 wt % aqueous solution of the k-carrageenan on an acrylate plate followed by evaporating water at 50°C in a humidity chamber with 80% humidity, k-carrageenan films were immersed in the respective 2 wt % of aqueous methanol (water/methanol ratio, 1/1) solutions of cationic polymers (poly{1,3-bis[4-alkylpyridinium]propane bromide}s) for 24 h, after which the films were taken out and dried at room temperature. The prepared membranes were 20 μm thick. The weight percents of the poly{1,3-bis[4-alkylpyridinium]propane bromide}s uptaken by the k-carrageenan films during the ion complex formation were calculated from the weight differences of k-carrageenan films before and after ion complex formation by dipping into the aqueous cationic polymer solutions, followed by drying were about 15 wt %.

Characterization

FT-IR

The chemical structures of the polyion complex membranes were characterized with an IR spectro-

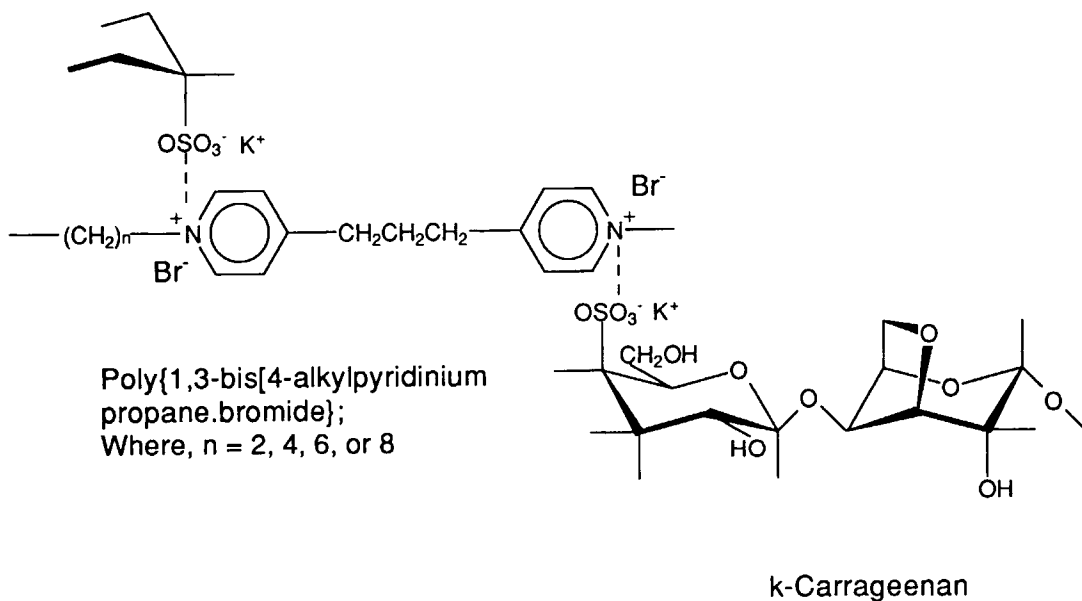


Figure 1 Chemical structures of the k-carrageenan (anionic polymer) and poly{1,3-bis[4-alkylpyridinium]propane bromide}s (cationic polymers) and schematic presentation of the polyion complex formation between them.

photometer (Bio-Rad, Digilab Division, model FTS-80, FTIR). The polyion complex membranes in film shape with 10 μm thickness, prepared by the same way mentioned above in the membrane formation, were used for obtaining the IR spectra.

X-Ray Diffractometry

To study the morphology of the prepared polyion complex membranes, an X-ray diffractometer (model D/MAX IIIB Rigaku) using nickel-filtered $\text{Cu-K}\alpha$ radiation with a wavelength of 1.54 \AA was used. The membrane thickness was around 20 μm . The experimental condition of the X-ray diffraction was always constant through this study as follows: Peaks File Listing: start 2θ : 2.00; stop 2θ : 50.00; step size: 0.004; scan speed: 2.000, and counting time 10.000.

Pervaporation Measurement

Pervaporation measurements were carried out by using a general pervaporation test cell, purchased from the Millipore Co. The membrane surface was 11.28 cm^2 and downstream pressure was 0.3 mmHg. The feed solution was a 90 wt % of ethanol-water mixture and the volume was 1 L. It ensures that the change of the feed composition is negligible during the time need for a pervaporation experiment. The pervaporation measurements were carried out at various feed solution temperatures (30, 40, 50, and 60°C). The total flux through the membrane was measured by weighing the liquid mixture removed from a reservoir. The partial flux and permeate vapor composition was determined by the analysis of the condensed permeate by a gas chromatograph (Perkin-Elmer 8500). The separation factor was defined as a follows:

$$\alpha = (W_{\text{H}_2\text{O}}/W_{\text{ethanol}})_{\text{Permeate}} / (W_{\text{H}_2\text{O}}/W_{\text{ethanol}})_{\text{Feed}}$$

where $W_{\text{H}_2\text{O}}$ is weight fraction of water, and W_{ethanol} is weight fraction of ethanol.

RESULTS AND DISCUSSION

Characterization of Membrane

FTIR

The FTIR spectrum of the polyion complex membrane made from k-carrageenan and poly{1,3-bis[4-butyl pyridinium]propane bromide} is shown in Figure 2. The FTIR spectrum of the polyion complex membrane shows the C—H stretch of pyridinium

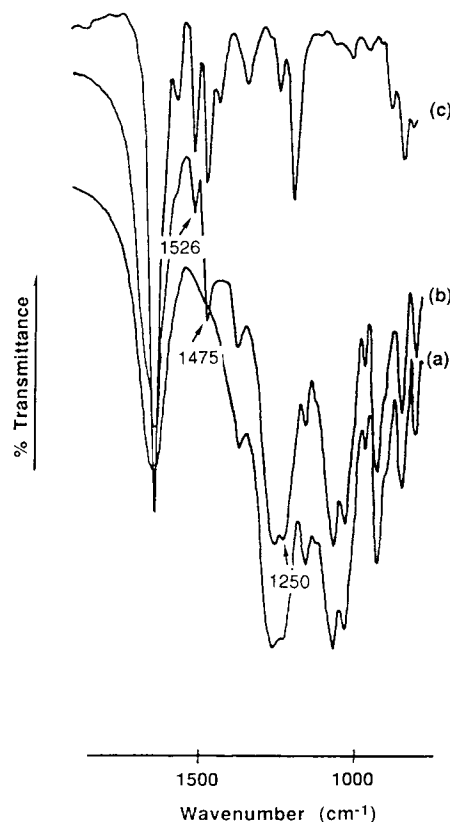


Figure 2 FTIR spectra of (a) the k-carrageenan film, (b) the polyion complex membrane, and (c) the poly{1,3-bis[4-butylpyridinium]propane bromide}.

at 1475 and 1526 cm^{-1} and S=O stretch of sulfate group at 1250 cm^{-1} . The C—H stretch of pyridinium group and the S=O stretch of sulfate group are from the cationic polymer (poly{1,3-bis[4-butyl pyridinium]propane bromide}) and anionic polymer (k-carrageenan) respectively, which are in ion complex state in the polyion complex membrane.^{6,7} The FTIR spectra of the other polyion complex membranes, prepared from different poly{1,3-bis[4-alkylpyridinium]propane bromide}s, were almost similar to one another, because the difference among the cationic polymers used in this study is only different numbers of methylene units between two ionic sites in a repeating unit.

Swelling Test

To confirm the cross-linking via the ion complex formation of the polyion complex membranes, the polyion complex membranes were heated in hot water. The polyion complex membranes were not dissolved but swelled, in spite of the uncross-linked k-carrageenan, and poly{1,3-bis[4-alkyl pyridinium]propane bromide}s were highly soluble in hot water.

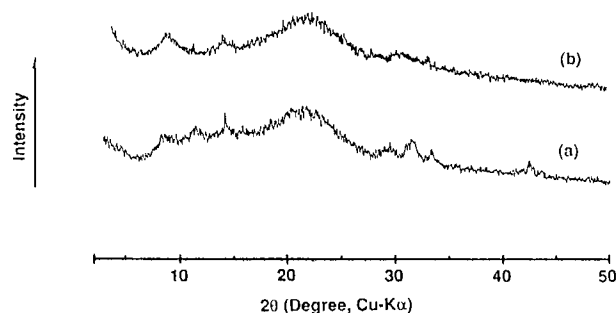


Figure 3 X-ray diffractograms of (a) the k-carrageenan film and (b) the polyion complex membrane made from k-carrageenan and poly{1,3-bis[4-butylpyridinium]propane bromide}.

After heating for 10 min at 90°C, it was found that only the surface layer of the membrane was cross-linked. Although the internal part swelled very much, the cross-linked surface part sustained in the very thin layer structure. This phenomenon might have resulted from the special way of cross-linking, ion complex formation, as well as the difficult interdiffusion of macromolecules of poly{1,3-bis[4-alkylpyridinium]propane bromide}s into the k-carrageenan film. In other words, macromolecules of poly{1,3-bis[4-alkylpyridinium]propane bromide}s could not go through the internal part of the k-carrageenan film because of the ionic interaction as well as the difficult interdiffusion of the two polymers in the ion complex formation process. As soon as the cations of poly{1,3-bis[4-alkylpyridinium]propane bromide}s met with the anions of k-carrageenan, ion complex (cross-linking) was formed and movement of the macromolecule of poly{1,3-bis[4-alkylpyridinium]propane bromide} into the k-carrageenan film became more difficult. Consequently, only the skin part of the k-carrageenan film was cross-linked. The thickness of the cross-linked layers of the membranes, calculated from the weight gains of the k-carrageenan films after ion complex formation in cationic polymer solutions, was about 3 μm .

Wide Angle X-Ray Diffractometry

Figure 3 presents the wide angle X-ray diffractograms of the k-carrageenan film and polyion complex membrane made from the k-carrageenan and poly{1,3-bis[4-butyl pyridinium]propane bromide}. Figure 3 indicates that the k-carrageenan film and the polyion complex membrane are in a totally amorphous state. It is interesting that the polyion complex membranes made from the totally amorphous k-carrageenan and highly crystalline poly{1,3-

bis[4-butyl pyridinium]propane bromide}¹¹ are totally amorphous. This result indicates indirectly that the two polymers are very homogeneously intermixed and in the ion complex state in the polyion complex membrane.

Pervaporation Separation of Water-Ethanol Mixture

The pervaporation separation of water-ethanol was carried out with a series of polyion complex membranes prepared by the method mentioned above from the k-carrageenan and respective poly{1,3-bis[4-alkylpyridinium]propane bromide}s (where alkyl was ethyl, butyl, hexyl, or octyl). Here, we rename the polyion complex membranes as follows for convenience: membrane 1 for the membrane made from poly{1,3-bis[4-ethylpyridinium]propane bromide}, membrane 2 for that made from poly{1,3-bis[4-butylpyridinium]propane bromide}, membrane 3 for that made from poly{1,3-bis[4-hexylpyridinium]propane bromide}, and membrane 4 for that made from poly{1,3-bis[4-octylpyridinium]propane bromide}. For the pervaporation separation of water-ethanol, 90 wt % aqueous ethanol was used as a feed mixture and the pressure of the vacuum side was kept constant at 0.3 mmHg. The operating temperature was varied: 30, 40, 50, and 60°C.

Effect of Temperature on the Water-Ethanol Separation

Figures 4 and 5 show total fluxes and separation factors in the separation of water-ethanol as a function of temperature through the polyion complex

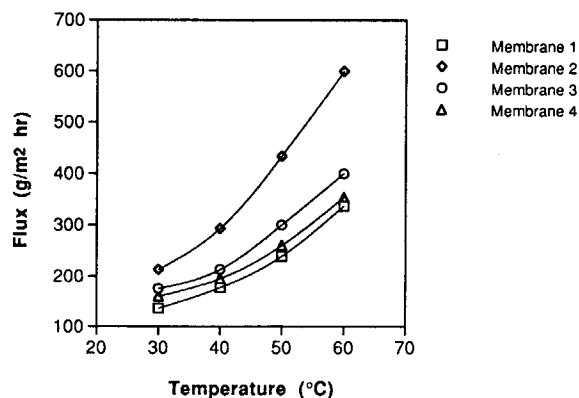


Figure 4 Total fluxes of the polyion complex membranes as a function of operating temperature in the pervaporation separation of water-ethanol of the 90 wt % aqueous ethanol solution.

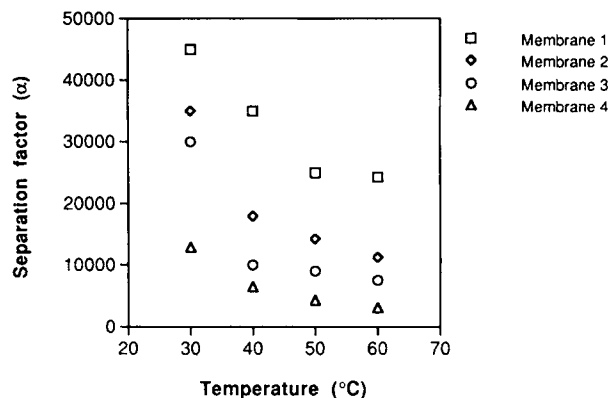


Figure 5 Separation factors of the polyion complex membranes as a function of operating temperature in the pervaporation separation of water-ethanol of the 90 wt % aqueous ethanol solution.

membranes, respectively. For the overall polyion complex membranes, the total fluxes and separation factors are very high. Especially, in the case of the membrane 2, total flux is over 600 g/m² h, with a separation factor of 12,000 at an operating temperature of 60°C. The high fluxes and high separation factors for the overall polyion complex membranes may be due to the excellent hydrophilicity of polyion complex and the rigid bulky main chain backbone structure of the k-carrageenan. The high fluxes are mainly due to the rigid bulky main chain structure of the k-carrageenan. Because the k-carrageenan, the major part of the membrane, is constructed with very rigid bulky main chain structure, the membrane has relatively high free volume. The relatively high free volume of the membrane is very favorable for the easy diffusion of permeants so that the membrane made from materials with high free volume shows high permeability. The high separation factors are basically due to the excellent hydrophilicity of the polyion complex layer of the polyion complex membrane. The excellent hydrophilicity of the polyion complex layer makes the film absorb water molecules very selectively. The selective absorption of water molecules is the determining factor for the high permselectivity.

From Figures 4 and 5, it is also found that the total fluxes increase drastically with increasing operating temperature, whereas the separation factors do not decrease much. The drastic increase with increasing temperature in the permeability without serious decrease in separation factor may result from the rigid bulky structure of the k-carrageenan and the excellent hydrophilicity of the polyion complex layer. Generally speaking, permeants absorbed into polymeric membranes act like plasticizers and in-

crease free volume with decreasing glass transition temperature of the membrane. Because the plasticizers increase the local motion of the membrane molecules, the bigger size molecules such as ethanol from the water-ethanol mixtures can easily penetrate into the membrane and diffuse out to the permeate side, which resulted in the decrease of permselectivity. This phenomenon is more distinctive at higher temperature, and the permselectivity is much lower at high temperature. However, in the case of the polyion complex membranes, because the membranes are made from k-carrageenan that has rigid bulky main chain, the glass transition temperature of them is very high and the water molecules absorbed into the membrane can not act as plasticizers to decrease seriously the glass transition temperature. Because of these properties, the polyion complex membranes show high permselectivity and permeability at high temperature.

Figure 6 shows that over a wide temperature range the experimental data closely obey the Arrhenius equation, and Table I presents the activation energies for the permeation of water and ethanol through the series of polyion complex membranes. The activation energies of water were in the range from 5.36 to 7.03 cal/mol °K and those of ethanol were in the range from 14.83 to 18.61 cal/mol °K.

Effect of Ion Contents on the Water-Ethanol Separation

Figures 7 and 8 present the effect of the ion contents of the polyion complex membranes on the total flux and separation factor. The ion contents of the polyion complex membranes were controlled by using different cationic polymers with different numbers

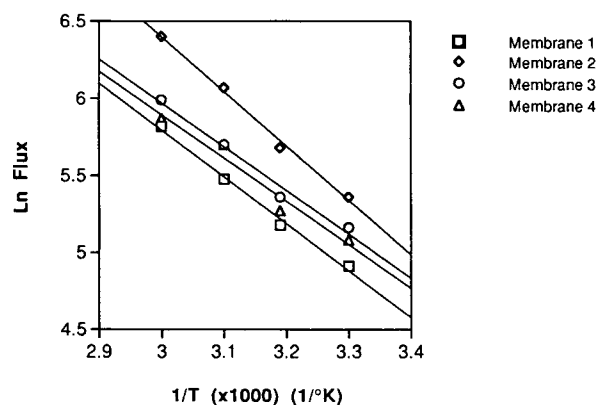


Figure 6 Arrhenius relationship between permeation flux and operating temperature in the pervaporation separation of water-ethanol of the 90 wt % aqueous ethanol solution through the polyion complex membranes.

Table I Activation Energies for the Permeation of Water and Ethanol Through the Polyion Complex Membranes

Membranes*	Activation Energy (Cal/mol °K)		
	Total Flux	Water	Ethanol
1	6.05	6.07	18.61
2	7.03	7.03	14.91
3	5.65	5.65	14.83
4	5.58	5.36	15.85

* Membranes were prepared by the ion complex formation between k-carrageenan and respective poly{1,3-bis[4-alkylpyridinium] propane. bromide}s in which alkyl was as a follow; ethyl for membrane 1, butyl for membrane 2, hexyl for membrane 3, and octyl for membrane 4.

of methylene units between two ionic sites per repeating unit, because the cationic polymers that have more methylene units between two ionic sites have lower ionic contents. To represent the ion contents, we used the number of methylene units of the cationic polymer. Therefore, membranes 1, 2, 3, and 4 have two, four, six, and eight methylene units per repeating unit of the used cationic polymer, respectively.

Figures 7 and 8 show the behaviors of the total flux and separation factors at operating temperature 30°C as a function of the number of methylene units between two ionic sites of the cationic polymers used in the formation of the polyion complex membranes. The total flux behavior through the polyion complex membranes as a function of the number of methylene units mentioned above is rather complicated. Membrane 1 with two methylene units shows the lowest flux, whereas membrane 2 with four methylene units shows the highest flux. In the range of number of methylene units from four to eight, the total flux decrease with increasing number of methylene units. On the other hand, the separation factor showed little different behavior from the total flux. The separation factors decrease gradually with increasing number of methylene units.

The decrease in the separation factor and total flux with increasing number of methylene units is probably due to the decreasing hydrophilicity of the polyion complex layer of the membranes. As the number of the methylene units of the cationic polymers used in the formation of polyion complex membranes increase, the hydrophobic part, i.e., alkyl chain, becomes longer and the hydrophilicity of the produced polyion complex layer will consequently decrease. This decrease in the hydrophilicity results

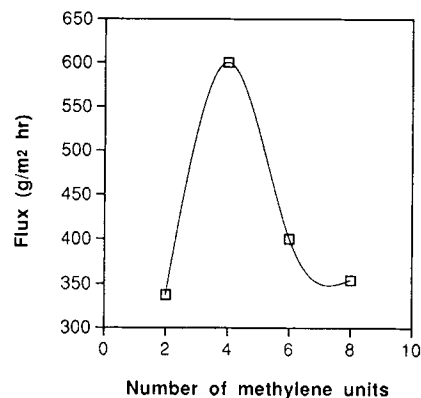


Figure 7 Total fluxes as a function of the number of methylene unit between two ionic sites of the cationic polymers used in the formation of the polyion complex membranes in the pervaporation separation of water-ethanol of the 90 wt % aqueous ethanol solution at 30°C.

in the decrease in the separation factor and total flux.

CONCLUSIONS

Polyion complex membranes based on k-carrageenan could be prepared by dipping the k-carrageenan film into the aqueous methanol solutions of cationic polymers. The polyion complex membranes are composed of polyion complex surface layers (about 3 μm in thickness) and k-carrageenan inside. The FTIR spectrum of the polyion complex membrane shows C—H stretch at 1475 and 1526 cm^{-1} and S=O stretch at 1250 cm^{-1} , which represent the pyridinium group and sulfate

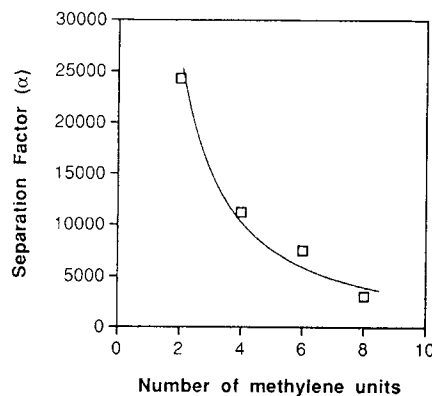


Figure 8 Separation factors as a function of the number of methylene units between two ionic sites of the cationic polymers used in the formation of the polyion complex membranes in the pervaporation separation of water-ethanol of the 90 wt % aqueous ethanol solution at 30°C.

group in the ion complex state, respectively. The WAXD result indicates that the polyion complex membranes are in totally amorphous state, which is good for high flux. For the pervaporation separation of water-ethanol, the polyion complex membranes show very high permselectivity and very high permeability over a wide temperature range because of the excellent hydrophilicity of the polyion complex surface layers and the relatively high free volume and high glass transition temperature of the k-carrageenan. The ion contents of the polyion complex layers of the membranes affect on the permselective properties such as permselectivity and permeability. The higher ion content is better for the higher permselectivity and higher permeability. For the water-ethanol mixture (90 wt % EtOH) at 60°C, the polyion complex membrane 2, made from k-carrageenan and poly {1,3-bis [4-butylpyridinium] propane bromide }, showed a separation factor of about 12,000 and 600 g/m² h of flux. With respect to the separation properties, this polyion complex membrane is highly comparable with the PAA/PCA-107 composite membrane (separation factor; 3,500 and flux 1.6 kg/m² h).⁷

REFERENCES

1. T. Hirotsu, K. Ichimura, K. Mizoguchi, and E. Nakamura, *J. Appl. Polym. Sci.*, **36**, 1717 (1988).
2. X. P. Zhao and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **41**, 2133 (1990).
3. W. Y. Chiang and C. M. Hu, *J. Appl. Polym. Sci.*, **43**, 2005 (1991).
4. R. Y. M. Huang and N. R. Jarvis, *J. Appl. Polym. Sci.*, **14**, 2341 (1970).
5. J. Hauser, G. A. Reinhardt, F. Stumm, and A. Heintz, *J. Membr. Sci.*, **47**, 261 (1989).
6. M. Tsuyumoto, H. Karakane, Y. Maeda, and H. Tsugaya, *Desalination*, **80**, 139 (1991).
7. H. Karakane, M. Tsuyumoto, Y. Maeda, and Z. Honda, *J. Appl. Polym. Sci.*, **42**, 3229 (1991).
8. J. Nieuwenhuis, Y. Y. Tan, and G. O. R. Alberda van Ekenstein, *Die Ange. Makromol. Chemie*, **147**, 83 (1987).
9. M. Yoshikawa, T. Yukoshi, K. Sanui, and N. Ogata, *Polym. J.*, **18**, 447 (1986).
10. M. Yoshikawa, S. Ochiai, M. Tanigaki, and W. Eguchi, *Makromol. Chem. Rapid Commun.*, **9**, 559 (1988).
11. J. G. Jegal, J. H. Kim, Y. I. Park, and K. H. Lee, *J. Appl. Polym. Sci.*, **54**, 65 (1994).

Received May 15, 1995

Accepted November 18, 1995