Characterization of Permeation Behaviors of Ethanol–Water Mixtures through Sodium Alginate Membrane with Crosslinking Gradient during Pervaporation Separation

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ABSTRACT: Dense sodium alginate (SA) membranes crosslinked with glutaraldehyde were prepared by a new solution technique, which had different extents of crosslinking gradient structures. The SA membranes having a crosslinking gradient structure were fabricated by exposing one side of the membrane to the reaction solution while blocking the other side by a polyester film to prevent the reaction solution from contacting it. The extent of the crosslinking gradient was controlled by the exposing time. When the swelling measurements were performed with uniformly crosslinked membranes in aqueous solutions of 70–90 wt % ethanol contents, it was observed that the crosslinking could reduce both the solubility of water in the membrane and the permselectivity of the membrane toward water. The pervaporation separation of the ethanol–water mixture of 90 wt % ethanol content was carried out with membranes with different extents of crosslinking gradients. As the crosslinking gradient was developed more across the membrane, the resulting flux as well as the separation factor to water was found to decrease while the membrane became stable against water. The pervaporation performances of the membranes with different membrane loadings in a membrane cell were also discussed using the schematic concentration and activity profiles of the permeant developed in them. The pervaporation separations of the ethanol/water mixtures through the membrane with an optimal crosslinking gradient were performed at different feed compositions and temperatures ranging from 40 to 80°C. The change in the membrane performance due to the relaxation process during pervaporation was observed with the operating temperature and feed composition. The relaxational phenomena were also elucidated through an analysis of the experimental data of the membrane performance measured by repeating the operation in a given temperature range. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1607–1619, 1998

Key words: sodium alginate; crosslinking gradient; pervaporation; separation of ethanol/water mixture

INTRODUCTION

Of the various membrane separations of liquid mixtures, the dehydration of organic–water mixtures by pervaporation has been investigated intensively because of their low energy consumption and high separation characteristics.[1,2] The membranes used in pervaporation have to be sufficiently selective and permeable to be of economical interest. However, compared to other membrane processes, the pervaporation process has a

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limit of the flux to which it can be reached because permeation can occur mainly by diffusion across the membrane thickness. Many efforts have been made to solve the problem. It is well known that hydrophilic polymers are selected as membrane material for the dehydration from various solvents because a water molecule is easily incorporated into the hydrophilic polymeric membrane. However, excess hydrophilicity of membrane material is not necessarily suitable for the dehydration process because it can give a low selectivity and poor membrane stability against an aqueous circumstance at the expense of high flux. When a highly permeable polymer material is selected, selectivity and membrane stability can be enhanced by chemical modification or crosslinking with the corresponding sacrifice of flux. Therefore, the membrane material should be modified to have the optimal combination of flux and membrane stability or selectivity.

Among the hydrophilic membranes, alginate membranes[3] are reported to present the most outstanding membrane performances for the dehydration of ethanol–water mixtures. In a previous work,[4] the outstanding membrane performance of the alginate membranes was reported to be attributed mainly to the excellent permselectivity to water in the sorption step. The performance of the sodium alginate (SA) membrane cannot be influenced only by process conditions like feed composition and temperature but also frequently by the relaxation of polymeric chains in the membrane. In particular, glassy polymers having a rigid and bulky structure tend to be stressed or relaxed depending on their thermal condition. The relaxation process takes place significantly near the glass transition temperature or glass transition concentration and it can make the material structure denser by the configurational rearrangement of the polymeric chains so that flux can be decreased correspondingly.[5–8] In the pervaporation process where a glassy polymeric membrane is employed for the dehydration of an aqueous mixture, different from other membrane processes is a pronounced anisotropic swelling developed in the membrane, by which a phase gradient can be established across the membrane thickness: a rubbery state at the feed-side membrane surface to a glassy state at the permeate-side surface.[4] The phase gradient would make a different relaxation process with the location in the membrane since relaxation can be expressed in terms of membrane mobility. To prepare a stable SA membrane against water, we also investigated the crosslinking reaction of SA with glutaraldehyde (GA).[9] It can be seen that the reaction took place between the hydroxyl groups of SA and the aldehyde groups of GA, and as the reaction progresses, the membrane stability is improved more but the permselectivity to water worsens. In this case, introducing the crosslinking gradient into the membrane structure can be worth considering as one of the methods to provide membrane stability as well as to minimize flux and permselectivity losses due to the crosslinking structure. In our previous study,[10,11] the permeation behavior of a permeant through the poly(vinyl alcohol) (PVA) membrane with a crosslinking gradient structure was discussed in relation to the profiles of permeant concentration and activity developed with the extent of the crosslinking gradient over the membrane thickness.

The purpose of this study was to prepare SA membranes with an optimal crosslinking gradient across the membrane thickness and to investigate the permeation behavior of permeants through it. To characterize the sorption behavior of the crosslinked SA membrane in the water–ethanol mixtures, the preferential sorption measurement of the membrane in the ethanol–water mixtures was carried out by a equipment which is able to precisely measure the concentration and amount of a liquid absorbed in the membrane. The permeation performance of the membrane having a crosslinking gradient structure will be discussed with the extent of the gradient and the membrane loading in the membrane cell. The optimal crosslinking gradient will be determined in terms of flux and membrane stability, and the pervaporation separations of the ethanol–water mixtures through the membrane will be investigated at different feed compositions and temperatures ranging from 40 to 80°C. The relaxational phenomena in the membrane during pervaporation will also be elucidated through an analysis of the experimental data of the membrane performance measured by repeating the operation at the given temperature.

EXPERIMENTAL

Materials

Sodium alginate (SA, extrapure grade) was purchased from Showa Chemical Inc. (Japan). Ethanol

(guaranteed reagent) was supplied by Merck (Germany). Glutaraldehyde (GA, 25% content in water, extrapure grade), hydrochloric acid (HCl, 35% content, extrapure grade), and acetone (guaranteed reagent) were purchased from Junsei Chemical Co. (Tokyo, Japan). Ultrapure deionized water was used. All chemicals were used without any further purification.

Membrane Preparation

A 2.5 wt % SA casting solution was prepared by dissolving SA in water. The casting solution was cast onto a thick polyester film with the aid of a Gardner casting knife and dried at room temperature in a fume hood for 1 day. Further drying was carried out in a heating oven at 100°C for 4 h. For the preparation of the membranes with a uniform crosslinking structure, the dry SA membrane was peeled off the polyester film and immersed at 40°C for 48 h in a reaction solution which contained 10 vol % of the GA solution and 0.05 vol % of HCl in acetone. For the fabrication of a membrane with a crosslinking gradient over the membrane thickness, the dry SA membranes on the polyester film were put into the reaction solution at 40°C for a given time. Herein, the crosslinking agent, the GA molecules, could diffuse from the exposed membrane surface toward the other side and, simultaneously, the crosslinking reaction took place between the aldehyde groups of GA and the hydroxyl groups of SA. The diffusing distance of the GA molecule would be determined by the exposing time, that is, the reaction time and, thus, the crosslinking gradient was developed in the membrane, depending on the reaction time. In all cases, after the crosslinking reaction, the membrane was taken out of the reaction solution, washed out several times with pure methanol, immersed in methanol for 24 h at 40°C to eliminate any possible residual HCl and GA, and then dried under a vacuum for 24 h. The thickness of the prepared membrane was 15–16 μm.

Infrared Measurement of the Prepared SA Membranes

Infrared spectra of the crosslinked SA membranes were measured with an FTIR spectroscope (Digilab FTS-80, Bio-Rad).

Measurements of Swelling Ratio and Preferential Sorption

To characterize the effect of crosslinking density on the sorption behavior of the SA membrane, the preferential sorption measurement of the membranes with a uniform crosslinking structure was carried out in ethanol–water mixtures using an equipment which is able to precisely measure the concentration and amount of a liquid absorbed in the membrane in equilibrium swelling. The membranes can be considered as an isotropic material.

In an isotropic material, since a change in the length due to swelling is the same in all directions, the ratio of the swollen length to the dry length of the membrane can be given by

$$R_L = \frac{L_x}{L_{xo}} = \frac{L_y}{L_{yo}} = \frac{L_z}{L_{zo}} = \frac{L}{L_o} \tag{1}$$

where L_x, L_y, and L_z are the dimensions of the swollen membrane in the x, y, and z directions, respectively, and the subscript o denotes the dry membrane. Therefore, the volume fraction of the solvent in the swollen membrane can be expressed in the following form[12]:

$$\phi = \frac{R_L^3 - 1}{R_L^3} = \frac{L_x L_y L_z - L_{xo} L_{yo} L_{zo}}{L_x L_y L_z} \tag{2}$$

The dense membranes were cut into a shape of slab with a dimension of 10 × 70 mm. The slabs were soaked in a 70–90 wt % ethanol content of the aqueous solutions for 2 days for equilibrium swelling. For the measurement of preferential sorption, the swollen slabs were taken out of the solution after the equilibrium swelling, wiped off with tissue paper as quickly as possible, and then placed into the glass tube X which, subsequently, was fitted to the device as shown Figure 1. While the glass tube was heated by the heating band, the liquids absorbed in the slabs were collected in the glass tube Y by liquid nitrogen under a vacuum with the valves B and C opened. The collected liquids were vaporized by applying heat on the glass tube Y with the valves B and D closed so that the region between the valves could be filled with the vapors of the liquids. The vapors were analyzed by a gas chromatograph (Shimadzu, Model GC-14B) which was equipped with an integrator (Shimadzu, Model C-R6A), two auto sample injectors, a thermal conductivity detector (TCD), a flame ionization detector (FID),

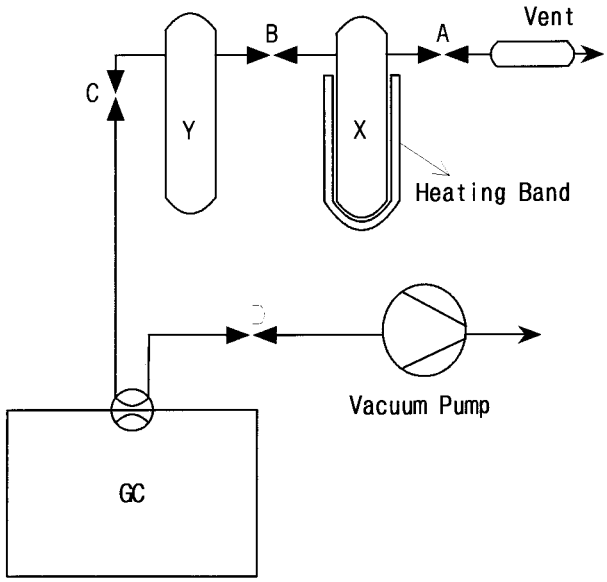

Figure 1 Schematic representation of desorption apparatus.

and two packed columns. Each sample injector was actuated by compressed air. The columns were 5 ft long with a 1/8-in. inside diameter packed with a Poropak Q. The vapors were automatically injected into the gas chromatograph by the injector. Ultrapure helium was used as the carrier. For measurement of the swelling ratio, the swollen slab was taken out and put on a paper wetted with the same solution, and then both ends of the slab were marked on the paper with a pen as quickly as possible and the distance L between the marks was measured with a Vernier caliper with an accuracy of ± 10 μm. After drying, the length L_o of the dry slab was measured. The solubility of the liquid in the swollen membrane ϕ was calculated by eq. (2). All measurements were repeated four or five times and the resulting data had standard deviation of $\pm 8\%$.

Pervaporation

The schematic pervaporation apparatus used in this study is illustrated in Figure 2. The membrane cell is made of stainless steel. A feed mixture enters the cell through the center opening, flows radially through the thin channel, and leaves the cell through the side opening, which allows a relatively high fluid velocity parallel to the membrane surface. The cell structure was depicted elsewhere.[10] The effective membrane area was 19.6 cm^2. The feed mixture was circulated from the feed tank having a capacity of 2.5 L through the membrane cell. The feed tank was wrapped with heating tape to heat the feed mixture. The feed mixture temperature was controlled by a PID temperature controller. The permeate pressure was controlled by the PID controller. The composition of the permeate vapor was determined by on-line gas chromatography (GC) analysis. The gas chromatography was the same as that used in the preferential sorption measurement. Thus, the permeate vapor could be injected directly into one of the columns by the injector for on-line measurement. The permeate vapor was collected in the cold trap by liquid nitrogen with a given time interval, heated to room temperature, and weighed to determine the flux. The separation factor was calculated by the following equation:

$$\alpha_{\text{water/ethanol}} = \frac{Y_{\text{water}}/Y_{\text{ethanol}}}{X_{\text{water}}/X_{\text{ethanol}}} \tag{3}$$

where X and Y are the weight fractions of each

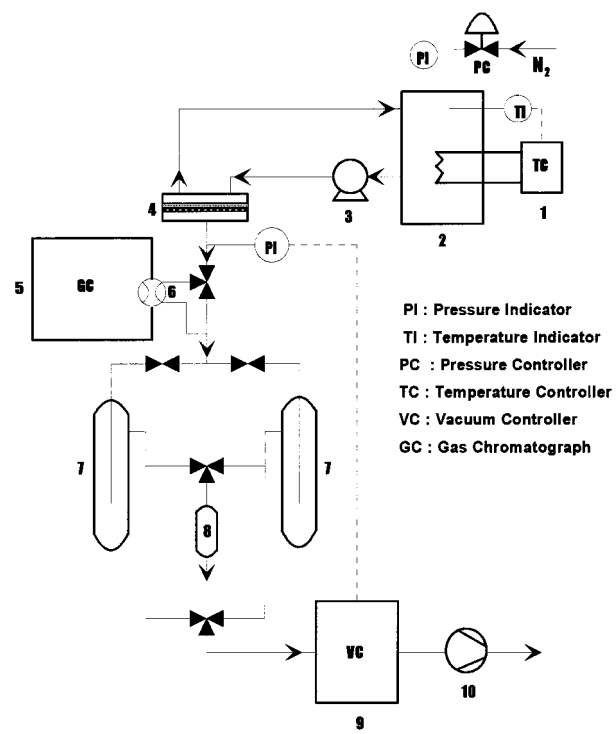

Figure 2 Schematic representation of pervaporation apparatus: (1) temperature controller; (2) feed tank; (3) pump; (4) membrane cell; (5) GC; (6) sample injector; (7) cold trap; (8) vent to atmosphere; (9) vacuum controller; (10) vacuum pump.

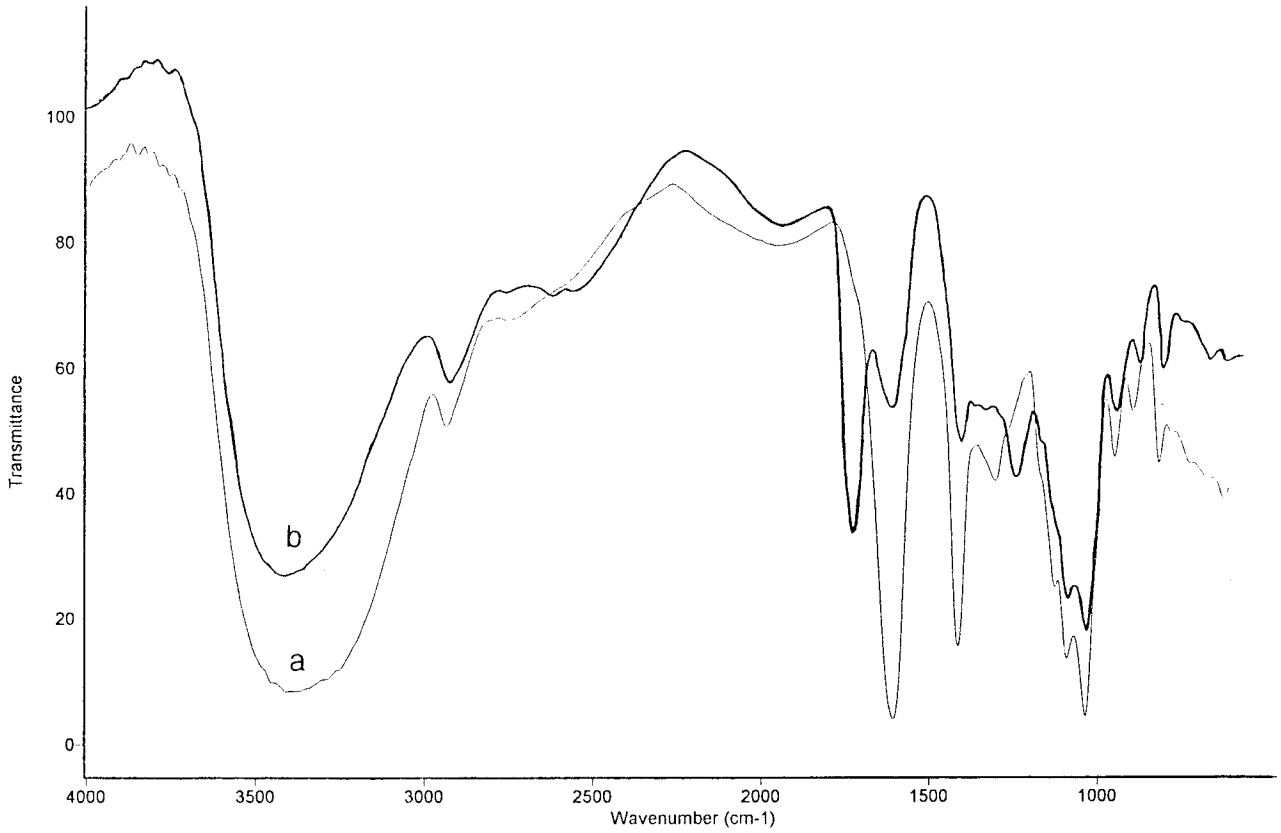

Figure 3 IR spectra of the nascent and crosslinked SA membranes: (a) nascent; (b) crosslinked.

component in the feed and permeate, respectively. To investigate the flux change by repeating the operation, the pervaporation run was repeated at different feed compositions in the temperature range of 40–80°C until the flux was not changed. In each run, the feed temperature was increased from 40 to 80°C in a sequence of temperature steps, and the measurements of the flux and separation factor were made every 10°C: After the measurement of the membrane performance at a temperature step, the feed mixture was heated to the next temperature step by a certain rate, and then after reaching the new temperature, the feed mixture was applied to the isothermal pervaporation experiment, and sample collection began 2 h later when the isothermal process proceeded to the steady state. Between the consecutive runs, the membrane was maintained at 40°C in the membrane cell with the permeate side vented to the atmosphere for 12 h. The heating rates employed were 1–0.7°C/min.

RESULTS AND DISCUSSION

IR Spectra Analysis

In a previous study,[9] the crosslinking reaction of SA with GA was characterized in a solution technique. In the solution technique, acetone, a nonsolvent of SA, was used as the reaction medium to prepare an undeformed and stable membrane during the reaction. GA was used as the crosslinking agent, and Hl, as the catalyst. The optimal composition of the reaction solution for preparing a stable SA membrane with a negligible acidification by HCl was determined to be 10 vol % of the GA solution and 0.05 vol % of HCl in acetone. In this study, the SA membrane was crosslinked under the optimal composition of the reaction solution. Figure 3 illustrates the IR spectra of the nascent and crosslinked SA membranes. The IR spectra exhibit the following two sets of significant changes in the peaks to confirm the reaction

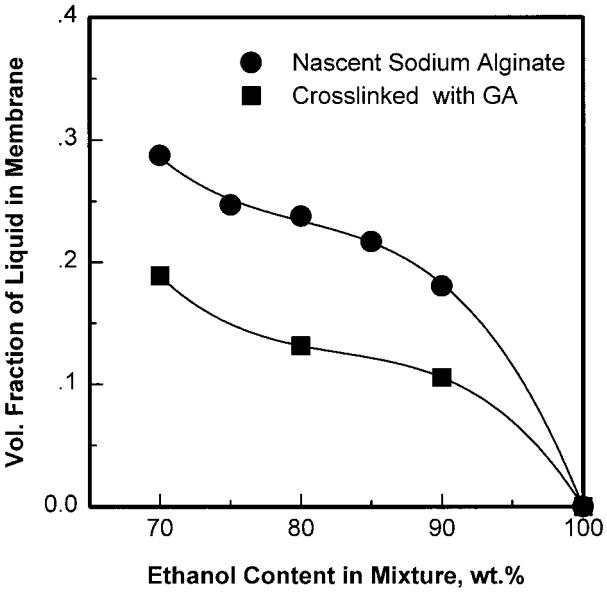

Figure 4 Volume fractions of liquid absorbed in the nascent and crosslinked SA membranes against ethanol content in mixture at 40°C.

between hydroxyl groups of SA and aldehyde groups of GA:

- Observing peaks at 1734 and 2700 cm^{-1} that are attributable to the characteristics of the aldehyde in the crosslinked membrane.
- After the reaction, a peak appearing at 1250 cm^{-1} which could be assigned to the formation of an acetal ring and ether linkage, resulting from the reaction between the hydroxyl groups of SA and the aldehydes of GA.

From the above spectral changes, the significant aldehyde peaks are found in the crosslinked membrane. There is little possibility of any residual GA in the membrane because it was removed from the membrane through washing and drying under a vacuum. Therefore, this set of aldehyde peaks can be only evidence for an unreacted aldehyde pendent to the SA chains, created by the monofunctional reaction of GA. Of the two aldehyde groups in a GA molecule, only one group participates in the reaction and is connected with to SA chain while the other remains unreacted and pendent to the SA chain. Therefore, it can be seen from the IR spectra that a monofunctional reaction as well as a bifunctional reaction of GA takes place in the reaction system of SA and GA. More detail on the IR characterization of the crosslinking reaction was explained elsewhere.[9]

Swelling Measurement

The preferential sorption properties of the nascent and uniformly crosslinked SA membranes were investigated in ethanol–water mixtures with different compositions and the results are as shown in Figures 4 and 5:

- As the water content of the mixture increases, the amount of the liquid absorbed in the swollen membrane increases and the ethanol content of the absorbed liquid also increases as much.
- When the membrane was crosslinked, the solubility of the liquid in the swollen membrane was reduced, whereas the ethanol content in the liquid was increased.

As the water content in the mixture increased, the hydrophilic membranes would attract more water molecules from the mixture so that the absorbed water could come with more ethanol molecules into the membrane by strong interaction between the water and ethanol molecules. This phenomenon is called "coupling sorption,"[12] which is why the solubility of the liquid and the ethanol content of the absorbed liquid increased with increasing water content in the mixture. As shown in these figures, the nascent SA membrane presents an excellent preferential sorption of water

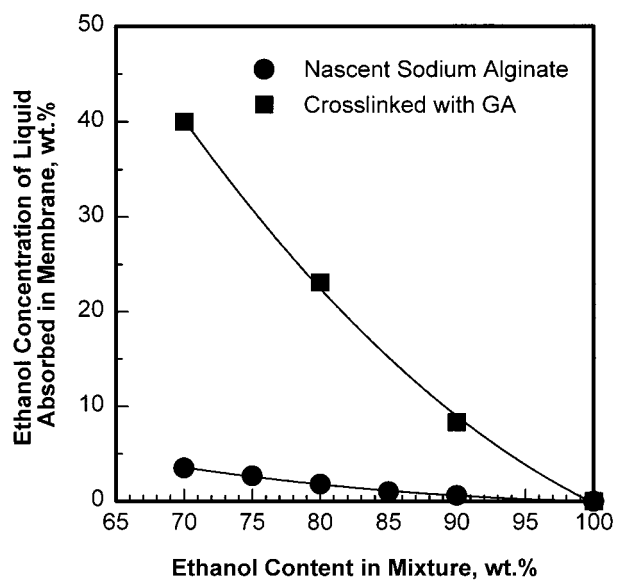

Figure 5 Ethanol contents of liquid absorbed in the nascent and crosslinked SA membranes against ethanol content in mixture at 40°C.

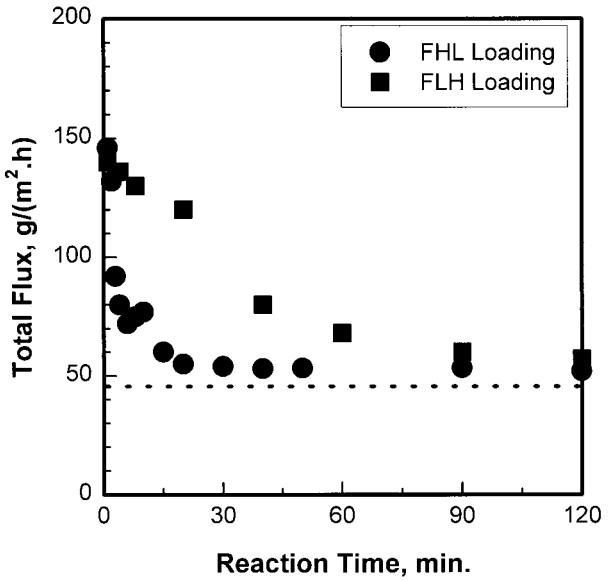

Figure 6 Flux change with reaction time at different membrane loadings in the membrane cell: reaction temperature, 40°C; feed composition, 90 wt % ethanol; operating temperature, 60°C.

because it possesses a very high affinity to water due to the salt functional groups attached to the SA chains. However, a more significant weight loss by slow extraction was observed during the swelling test in a higher water content of the mixture, that is, the membrane stability of the membrane against water was poorer at a higher water content in the mixture. Thus, the modification of the nascent membrane should be needed to enhance the membrane stability in a wide range of feed composition. One of methods to enhance membrane stability is crosslinking. Usually, a polymeric material with a higher crosslinking density has a more compact network structure and less solubility of liquids. Thus, it is clear that the reduced liquid solubility in the crosslinked membrane in Figure 4 results from the crosslinked structure in the membrane. GA is miscible in both water and ethanol, indicating that the aldehyde group has an affinity to both of them. In addition, it is reported that the acetal group has a good affinity toward alcohol rather than toward water.[13] From these facts, it can be seen that the crosslinked SA membrane will have less affinity to water, that is, less preferential sorption of water as shown in Figure 5. The acidification of some of the salt groups by HCl is likely to reduce the number of the salt groups in SA. The acidified SA, that is, alginic acid, is insoluble in water. However, the SA membrane treated with only the reaction solution containing no GA was soluble in water. It reveals that the acidification must be not significant in the reaction system of this study.

Pervaporation

Effect of Crosslinking Gradient

When a nascent SA membrane with one surface blocked by a polyester film was put into the reaction solution, a crosslinking gradient would be developed in the membrane by diffusing the crosslinking agent molecules from the contacting surface to the other end of the membrane. The extent of the crosslinking gradient was controlled by adjusting the exposing time, for example, the reaction time to the reaction solution. The effect of the crosslinking gradient structure has already been well described in ref. 10. The pervaporation separation of a water–ethanol mixture was performed through the membranes fabricated at various reaction times. The results are exhibited in Figures 6 and 7. The membrane performance was found to be quite dependent on which membrane surface is in contact with the feed mixture, that is, the FHL (feed in contact with a membrane surface having high crosslinking density) or the FLH (feed in contact with a membrane surface having

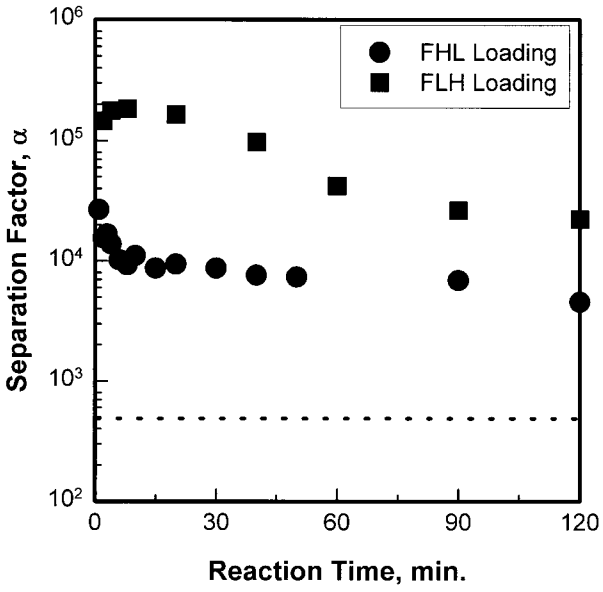

Figure 7 Change in separation factor with reaction time at different membrane loadings in the membrane cell: reaction temperature, 40°C; feed composition, 90 wt % ethanol; operating temperature, 60°C.

low crosslinking density). In the case of loading the membrane in the FHL direction, the flux decreased rapidly with the reaction time and then decreased less and less until 20 min and then almost leveled off or slightly decreased, while the separation factor decreased dramatically until 20 min and then decreased slightly with the reaction time. The change of the flux with the reaction time might be explained that once the crosslinking takes place at the membrane surface layer the crosslinking density in the layer increases with the reaction time to make the zone more compact and rigid so that the reaction and the transport of the crosslinking agent molecule can be more controlled by the diffusion of the crosslinking agent molecules through it. Looking at the swelling experimental result, the crosslinked SA membrane has a lower permeant concentration and less preferential sorption toward water than has the nascent membrane, which would cause less of a separation factor for the dehydration process. On the other hand, when the membrane was loaded in the FLH direction, it is very interesting to note that the flux showed a slight decrease with the reaction time, while the separation factor was not changed, almost constant for first 20 min of the reaction time, and then started to decrease with the reaction time. From these observations, all the membranes are believed to have a crosslinking gradient structure to a different extent and it can be postulated that it may take more than 20 min for the crosslinking agent molecules to move to the opposite end. Based on the parameters and profiles determined in our previous study, a schematic representation of the possible concentration and activity of the permeant in the SA membrane with different crosslinking gradients could be as given Figure 8. When the permeate pressure is well below the saturated vapor pressure of the permeants, the permeant concentration at the permeate side-membrane surface equals zero and the flux can be given by the following simplified equations:

$$Jt = \int_0^{C_{m1}} D(C)dC = D_{\text{ave}}C_{m1} \tag{4}$$

$$D_{\text{ave}} = \frac{\int_0^{C_{m1}} D(C)dC}{\int_0^{C_{m1}} dC} = \frac{Jt}{C_{m1}} \tag{5}$$

where J is the flux; t, the membrane thickness;

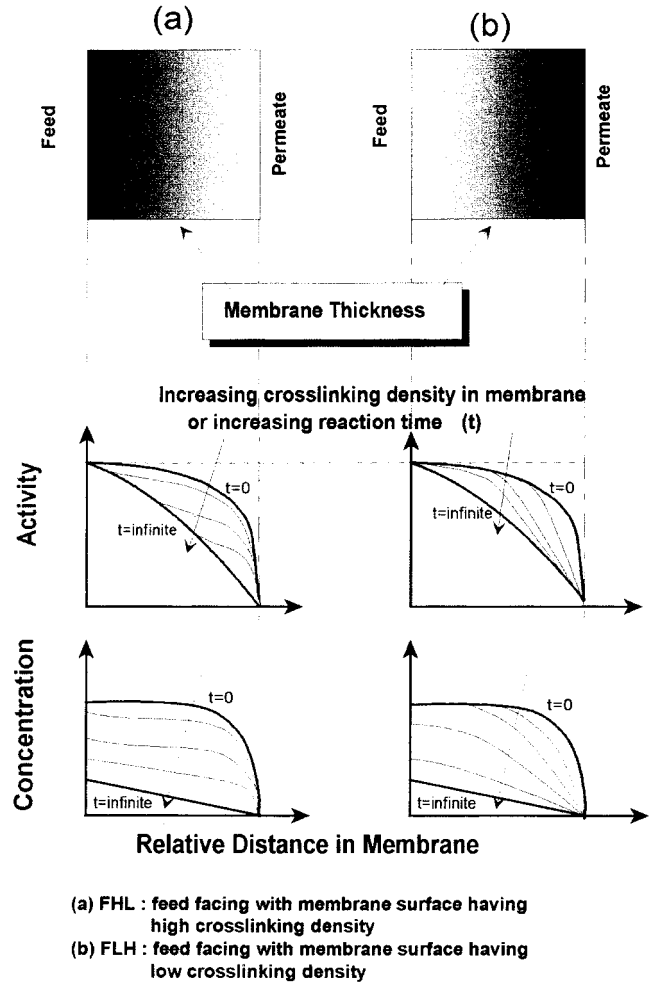

Figure 8 Schematic representation of possible concentration and activity profiles of permeant in the membrane with crosslinking gradient.

$D(C)$, the concentration-dependent diffusivity of the permeant; C, the concentration of the permeant in the membrane; C_{m1}, the concentration of the membrane surface at the feed side; and D_{ave}, the average diffusivity of the permeant in the membrane, which is a function of the overall concentration of the permeant involved in the membrane. The overall concentration C_{ov} is the average concentration across the membrane thickness, which could be determined from an area surrounded by the concentration curve as follows:

$$C_{\text{ov}} = \frac{\int_0^1 Cdx}{\int_0^1 dx} \tag{6}$$

where x is the relative distance from the feed-side membrane surface in the thickness direction. Usually, the concentration-dependent diffusion coefficient increases with the permeant concentration in the membrane due to the plasticization action of the permeant molecules on the polymeric chains in the membrane.[14] In eq. (4), the flux is proportional to the product of the average diffusivity and solubility of the permeant in the membrane at a given membrane thickness. In Figure 8, with increasing reaction time, C_{m1} and C_{ov} in the FHL loading decrease because of the greater crosslinked membrane surface exposed to the reaction solution, while C_{m1} and C_{ov} in the FLH loading do not decrease as much as in the FHL loading because fewer crosslinking agent molecules reach the surface blocked by the polyester film and the resulting crosslinking density can be much lower in the given range of reaction time. As a result, with increasing reaction time, the flux in the FLH loading could decrease less with the reaction time and always be higher than that in the FHL loading. The dotted lines in Figures 6 and 7 represent the flux and separation factor of the membrane with a uniformly crosslinked structure fabricated in the same reaction solution, respectively. The fact that the level-off values in the FHL loading could not approach the dotted lines in these figures can be evidence of a nonuniform membrane structure attributed to a difficulty in diffusing the crosslinking agent molecules through the rigid and compact surface layer which is exposed to the reaction solution.

The validity of the membranes with a crosslinking gradient structure proposed in this study is to minimize the flux and permselectivity losses as well as to give the hydrophilic membrane enough stability against the aqueous feed. The membrane with a crosslinking gradient could have enhanced selectivity and flux in the separation of the liquid mixture, compared with the membrane with a uniformly crosslinked structure, but it has a lower membrane performance and better membrane stability than has the nascent membrane. Thus, the crosslinking gradient should be optimized in terms of the optimal combination of the membrane stability and membrane performance. The systematic optimization of the gradient can be made by controlling the concentration or activity profile of each permeant of the mixture developed in the membrane as described in the previous study[7] because a difference in the concentration profiles of each component in the membrane may give rise to the separation of a liquid mixture. Many precisely controlled works are needed for that. However, the optimal reaction time was approximately determined in this study; when the exposing time was longer than 5 min, the resulting membrane was stable enough in water while the membrane performance was observed relatively acceptable at an exposing time of less than 15 min from Figures 6 and 7. Thus, the optimum reaction time is likely to be about 10 min in terms of membrane stability in an aqueous condition as well as in terms of membrane performance.

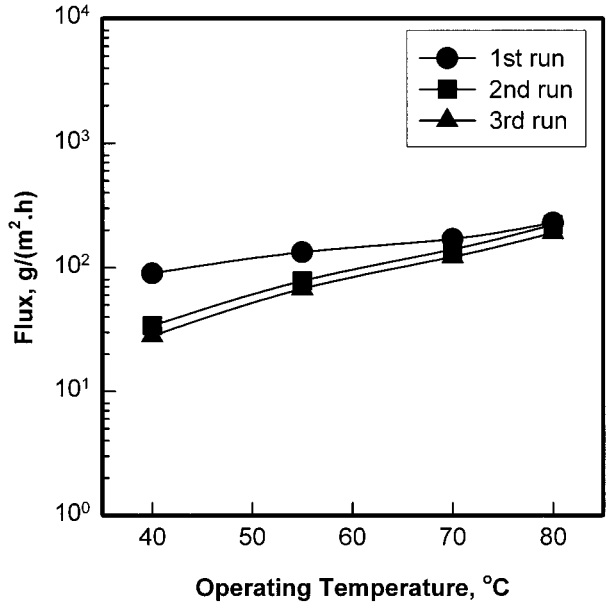

Figure 9 Plot of flux of the SA membrane having crosslinking gradient (reaction time, 10 min) against operating temperature in repeating operation: feed, 90 wt % ethanol.

Effect of Feed Composition and Temperature

All the membranes with the optimal crosslinking gradient structure used in this study were prepared in the same batch to ensure that identical thermal histories are imposed on them before measuring the membrane performance. Fluxes and separation factors measured with the membranes through several consecutive runs at a 90 wt % ethanol content of the feed were plotted with the operating temperature in Figures 9 and 10, respectively. In all cases, the membranes were loaded in the membrane cell in the FHL direction, which could make the highly crosslinked surface

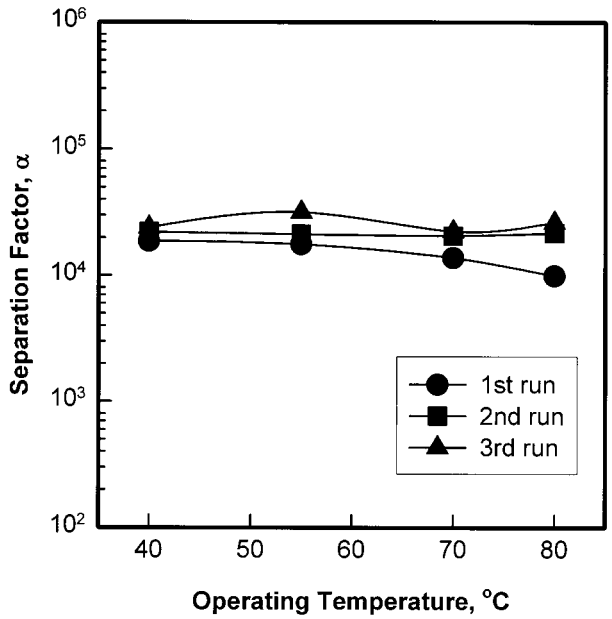

Figure 10 Plot of separation factor of the SA membrane having crosslinking gradient (reaction time, 10 min) against operating temperature in repeating operation: feed, 90 wt % ethanol.

face the feed mixture for membrane stability. The change in membrane performance could be observed in repeating the run. With repeating the run, the flux at a certain temperature decreased dramatically at the second run, decreased less at the third run, and then almost leveled off after the third run. The flux change was more significant when the operating temperature was lower. These phenomena had already been observed in the previous work where the pervaporation separation of an ethanol–water mixture was performed with a nascent SA membrane.[4]

The decrease of flux with repeating the run can be explained to be due to the relaxation process occurring in the membrane during each run. The relaxation process is a configurational change of polymeric chains taking place only in glassy material. In the pervaporation process using a glassy membrane, the phase gradient can be developed in the membrane from the rubbery state to the glassy state through the transition state. The relaxation process can occur faster in a material with higher mobility. Thus, in this study, it could be postulated that the relaxation rate might be fast in the beginning stage or at the first run, and then with operating time or repeating the run, the relation rate decreases more rapidly to zero where the relaxation time is too long for the experimental time scale. On the other hand, with increasing temperature, the membrane mobility is higher so that the membrane can undergo a greater extent of relaxation in the beginning stage before measuring flux and then be subjected to a slower relaxation regime, resulting in a smaller extent of relaxation progressing over most of the measuring time. Thus, in the next run, flux showed a pronounced decline at the lowest temperature and then the flux was less changed with increasing temperature. Evidence for the relaxation process could be supported by the increase in the separation factor with repeating the run (Fig. 10). As discussed above, the relaxation comes with the densification of the membrane structure by which the selectivity of the resulting membrane can be enhanced.

Figure 11 presents Arrhenius plots of the fluxes measured first through two consecutive runs against the operating temperature at different feed compositions. The fluxes in more than three runs could not be plotted because of too little change of the membrane performance to distinguish themselves from the others. Apparently, a significant change in the flux was found to take place at a high ethanol content of the feed with repeating the run. More detail can be obtained through an analysis of the permeation activation

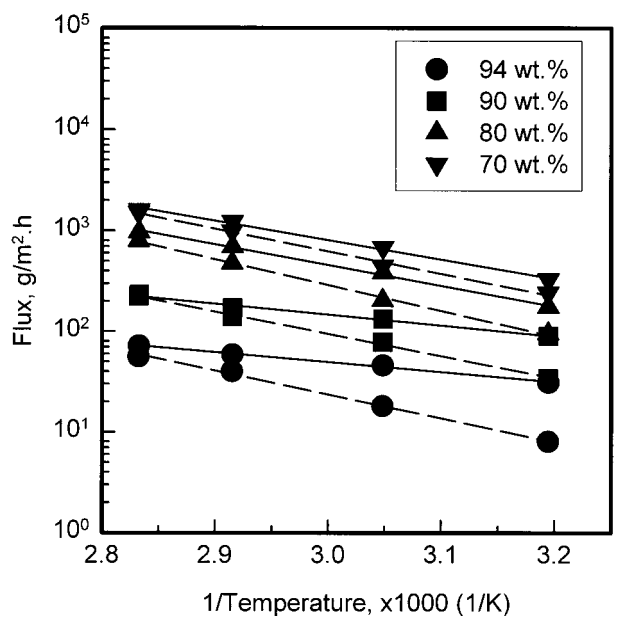

Figure 11 Arrhenius plots of flux through the SA membrane having crosslinking gradient (reaction time, 10 min) against temperature at different feed compositions: (solid line) first run; (dotted line) second run.

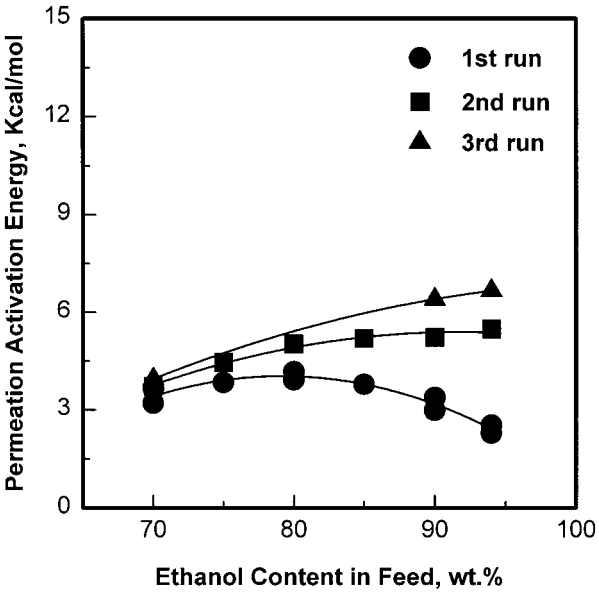

Figure 12 Permeation activation energy of the SA membrane having crosslinking gradient (reaction time, 10 min) with feed composition at different runs.

energy data. The permeation activation energies were determined from the slope of each line and plotted with the feed composition as shown in Figure 12. According to the "solution–diffusion model," the permeation activation energy (E_p) can be expressed as a function of the heat of sorption (ΔH_s) and the diffusion activation energy (E_d) as follows:

$$E_p = \Delta H_s + E_d \tag{7}$$

When the ethanol content in the feed is higher, the solubility and diffusivity of the permeants become smaller and require high activation energies in both sorption and diffusion steps as discussed above. Thus, the permeation activation energy should increase with the ethanol content in the feed. However, the experimental result showed a parabolic shape of the permeation activation energy curve in the first run, which is an deviation from what is expected. The deviation may result from the relaxation process, depending on the feed composition.

In a previous article,[4] the relationship between the relaxation rate and membrane mobility was thoroughly examined: When membrane mobility is high, relaxation is fast in the beginning and then very slow, while relaxation can occur slowly and continuously with time in a membrane with lower mobility. The relaxation made the permeation activation energy increase because of the densification of the membrane structure. At a lower ethanol content in the feed, membrane mobility becomes greater because of the significant plasticization action of the permeants absorbed in the membrane so that the relaxation can occur faster and more in the beginning, followed by slow relaxation over the rest of the process period, which is why the permeation activation energy increases with decreasing ethanol content until a certain ethanol content and then decreases by a remarkable increase in membrane mobility due to higher sorption of the permeants, domineering the effect of membrane mobility by more sorption over that of relaxation on the activation energy. The permeation activation data obtained in the second run could confirm this postulation. The permeation activation energy in the second run was observed to increase more at a higher ethanol content in the feed as a result of the continuous and slow relaxation process.

Fluxes obtained in the steady state are plotted with the feed composition at different operating temperatures in Figure 13. The flux data with the feed composition present a normal trend as in the permeation of aqueous ethanol through hydrophilic membranes: a smaller flux at a higher ethanol content in the feed and a higher flux at higher temperature. However, there is no specific ten-

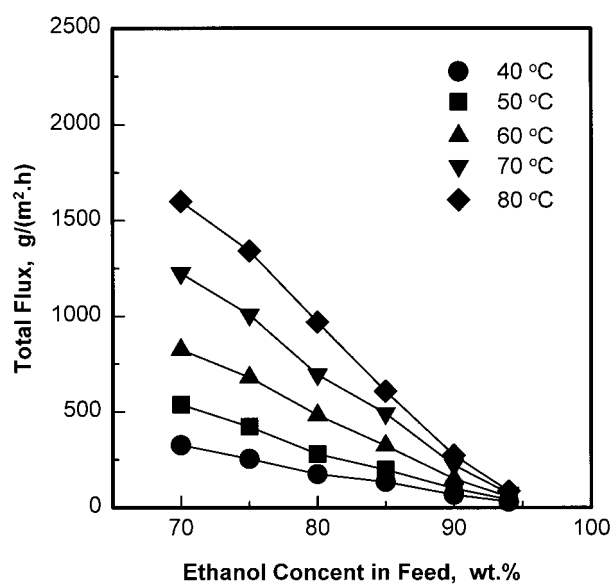

Figure 13 Plots of total fluxes in steady state through the SA membrane having crosslinking gradient (reaction time, 10 min) with feed composition.

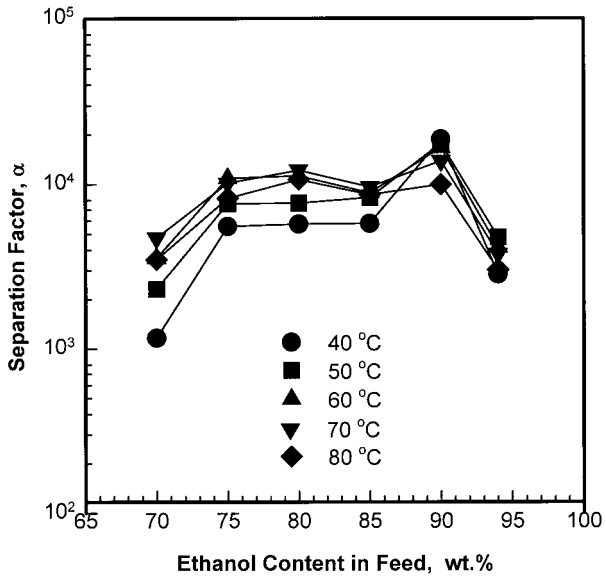

Figure 14 Plots of separation factors through the SA membrane having crosslinking gradient (reaction time, 10 min) with feed composition.

dency in the separation factor with the feed composition (Fig. 14). It is interesting to note that, with increasing temperature, the separation factor increases until a certain temperature and then decreases. For feed composition beyond 90 wt % ethanol content, the separation factor declined. The reason for that is not clear but the former might be explained in terms of the relaxational behavior of polymeric chains. At higher temperature, membrane mobility becomes greater and is more likely to cause the relaxation process and to make the membrane structure more compact by the configurational rearrangement of polymeric chains, so that the separation factor will be higher, but when the temperature is higher than a certain temperature, the motion of polymeric chains is so active that the resulting membrane structure can be loose enough to decrease the separation factor with temperature, domineering over the effect of the relaxational process. When the ethanol content in the feed is higher, the sorption of liquid permeants is diminished and the plasticization of the absorbed permeants in the membrane becomes feeble. Finally, a point can be reached where the feed mixture will be in a nonsolvent circumstance for the membrane material. When the ethanol content increases beyond the point, the membrane would not be swollen but consolidated without any phase gradient across the membrane during pervaporation and, thus, the selectivities in both the sorption and diffusion steps would be less pronounced.

CONCLUSIONS

For the pervaporation separation of an ethanol–water mixture, SA membranes having a crosslinking gradient structure were prepared to provide membrane stability as well as to minimize flux and permselectivity losses by a crosslinked structure. The SA membranes were fabricated by a solution technique where GA was the crosslinking agent, and HCl, the catalyst for the crosslinking reaction, and acetone was used as a reaction medium instead of aqueous salt solutions.

To characterize the selective sorption behavior of the crosslinked SA membrane in the water–ethanol mixtures, swelling measurements of the membrane in the ethanol–water mixtures of 70–90 wt % ethanol content were carried out. From the swelling measurement, it was observed that crosslinking could reduce both the solubility of water in the membrane and the permselectivity of the membrane toward water, although membrane stability was enhanced.

SA membranes having a crosslinking gradient structure across the membrane thickness were prepared by immersing the nascent SA membrane, one side of which was blocked by a polyester film, in the reaction solution. The extent of the gradient was controlled by the exposing time, that is, the reaction time. When the membrane surface having a high crosslinking density was in contact with the feed mixture, in the beginning, the flux decreased rapidly with increasing reaction time until 30 min and then almost leveled off or slightly decreased while the separation factor decreased constantly. The level-off value was higher than the flux of a uniformly crosslinked membrane due to a nonuniform membrane structure which can be equivalent with a less crosslinked membrane. The optimal reaction time was determined approximately 10 min in terms of membrane stability and membrane performance.

The pervaporation separations of the ethanol–water mixtures through the membrane with the optimal crosslinking gradient were performed at different feed compositions in the temperature range of 40–80°C. A significant decline in the flux and a slight increase in selectivity were obtained by the relaxation taking place in membrane during pervaporation.

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