

A Study on Permeation Behavior of a Liquid Mixture Through PVA Membranes Having a Crosslinking Gradient Structure in Pervaporation

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SYNOPSIS

Two types of dense poly(vinyl alcohol) (PVA) membranes crosslinked with glutaraldehyde were prepared by a new solution technique: membranes with uniform crosslinking structure and with crosslinking gradient structure. From the permeation of pure water through a membrane having a uniform crosslinking structure, the effect of crosslinking density in the membrane on the permeation activation energy, plasticizing coefficient, and diffusivity of the permeant was investigated. The concentration and activity profiles of the permeant in the membrane in the pervaporation process were determined using the diffusion equation and Flory–Huggins thermodynamics. PVA membranes having a crosslinking gradient structure were fabricated by exposing one side of the membrane to the reaction solution while the other side was blocked by a polyester film to prevent the reaction solution from contacting it. The extent of the gradient was controlled by the exposing time. The pervaporation separation of the water–acetic acid mixture was carried out on the membrane having a crosslinking gradient structure, and the pervaporation performance with different membrane loading in the membrane cell was discussed using a schematic concentration and activity profiles of the permeant which was made based on the results from the permeation of a pure component through the membrane with a uniform crosslinking structure.

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INTRODUCTION

Most of the technical efforts in the development of membrane separation processes have involved the selective removal of a specific component from the liquid mixture. Of the various membrane separations of the liquid mixtures, dehydrations of organic–water mixtures by pervaporation have been investigated intensively because of 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. For the dehydration, many polymers have been screened as potential membrane materials, and excellent re-

sults have been obtained with membranes prepared from hydrophilic polymers, such as poly(vinyl alcohol).

Compared to other membrane processes, the pervaporation process has a limit of the flux to which it can reach because the permeation of permeants occur mainly by diffusion across the membrane thickness. Much effort has been made to solve the problem. However, since a membrane with a high flux gives a low selectivity, two strategies can be employed to develop membranes with an optimal combination between permeation and selectivity:

- If one starts with a highly selective membrane material, the flux can be improved by increasing the operating temperature or/and decreasing the effective membrane thickness through two

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types of membranes, namely: (1) integrally skinned membranes,³⁻⁵ in which the top layer and support layer originate from the same material, and (2) composite membranes,⁶⁻⁸ where the top layer and support layer consist of different materials.

- If a highly permeable polymer material is selected, selectivity can be enhanced by chemical modification,^{8,9} crosslinking,^{10,11} or blending with other polymers.¹²

On the other hand, Koops et al.⁶ suggested a dense bilayer membrane consisting of a dense poly(vinyl alcohol) (PVC) layer on top of a dense PAN layer to achieve extremely high selectivities even though the fluxes were relatively low, and they explained the permeation of water-acetic acid through the membrane in terms of the concentration profiles of permeants developed in the membrane with the help of the so-called exponential six-parameter model. The concentration or activity profiles of permeants developed in the membrane will be affected by the membrane structure as well as by the membrane material. These profiles affect significantly the membrane performance. Usually, when the membrane is more swollen in the feed mixture or less crosslinked, the profiles have more convex shapes. Thus, the concentration and concentration-dependent diffusivity of the permeant in the membrane can be larger, leading to larger flux and smaller selectivity due to significant coupling fluxes.¹³

The purpose of this study was to investigate the permeation behavior of permeants through PVA membranes having different crosslinking gradients developed across the membrane thickness. To analyze the permeation behavior, basic parameters will be obtained from the permeation of the pure component through the PVA membrane with a uniform crosslinking structure. The permeation behavior is discussed in relation to the profiles of the permeant concentration and activity developed with the extent of the crosslinking gradient over the membrane thickness. In the preparation of crosslinked PVA membranes, a nonsolvent of PVA, acetone, was used as a reaction medium instead of aqueous salt solutions to prepare a stable shape of the membrane. Glutaraldehyde and HCl were used as a crosslinking agent and a catalyst for the reaction, respectively. The details of this method have been well described elsewhere.¹⁴

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) was purchased from Aldrich Chemical Co. The average molecular weight and saponification of the PVA were 50,000 and 99%, respectively. Glutaraldehyde (GA) (25% content in water, extrapure grade, which is called the GA solution hereafter), hydrochloric acid (35% content, extrapure grade), acetone (guaranteed reagent), and acetic acid (guaranteed reagent) were purchased from Junsei Chemical Co. (Tokyo, Japan). Ultrapure deionized water was used. All chemicals were used without further purification.

Preparation of PVA Membranes with Crosslinking Gradient

Base membranes were prepared from a casting solution containing 10 wt % PVA, 0.5 vol % GA solution, and 0.12 vol % HCl in water. The resulting 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. The base membranes fabricated thereby were slightly crosslinked but they possessed enough stability in aqueous solutions. For preparation of membranes with a uniform crosslinking structure, the base membrane was peeled off the polyester film and immersed at 40°C for 48 h in a reaction solution which contained a different content of GA solution, acetone, and HCl. The GA solution content in the reaction solution ranged from 0 to 5 vol %. For the fabrication of a membrane with a crosslinking gradient over the membrane thickness, the base membranes on the polyester film were put into a reaction solution containing 5 vol % of GA solution at 40°C for a given time. Herein, the crosslinking agent, 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 PVA. The diffusing distance of the GA molecule would be determined by the exposing time, i.e., 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 water, immersed in pure water for 24 h at 40°C to eliminate any possible residual HCl and GA, and then dried under vacuum for 24 h. The membrane thickness prepared was 12–14 μm .

Swelling Measurements

The swelling ratio can be measured from changes in length before and after equilibrium swelling for the uniformly crosslinked membranes which go through an isotropic length change during the swelling process.¹³ Dry membrane strips were immersed in both water and acetic acid thermostated at 40°C for 48 h to allow the strips to reach an equilibrium sorption. After measuring the swollen length, l , of a strip at equilibrium sorption, the strip was dried for 30 h at room temperature under vacuum and then the dry length, l_0 , was measured. The swelling ratio, R , and the volume fraction of liquid absorbed in the swollen membrane, v , are defined as

$$R = \frac{l}{l_0} \quad (1)$$

$$v = \frac{R^3 - 1}{R^3} \quad (2)$$

Pervaporation Experiments

Pervaporation tests were carried out for the permeations of pure water and the water-acetic acid

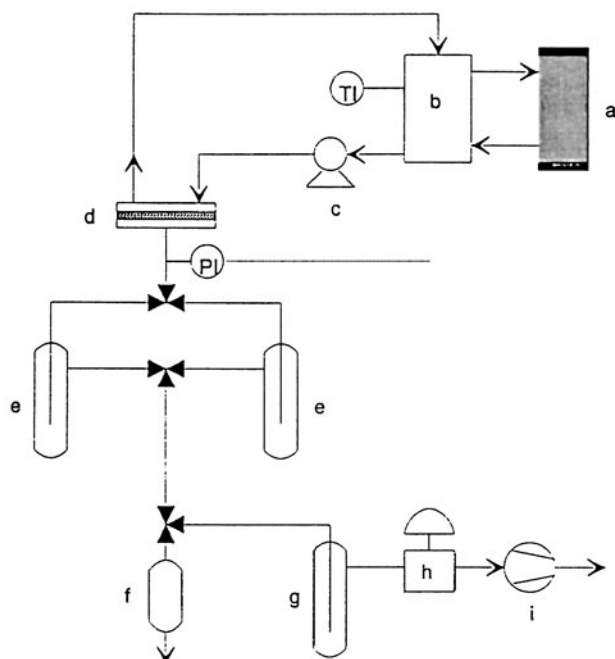


Figure 1 Schematic representation of pervaporation apparatus: (a) water bath; (b) feed tank; (c) pump; (d) membrane cell; (e, g) cold trap; (f) vent to atmosphere; (h) vacuum controller; (i) vacuum pump.

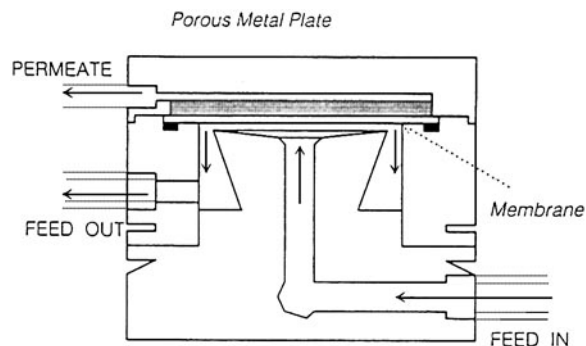


Figure 2 Schematic presentation of membrane cell.

mixture through the PVA membranes with a uniform crosslinking structure and with a crosslinking gradient structure, respectively. A schematic diagram of the pervaporation apparatus used is depicted in Figure 1. Feed was kept at the selected temperature by a thermostated water bath. The feed was continuously circulated from the feed tank through a membrane cell by a pump (Model D25, Precision Scientific Inc., Chicago, IL). The membrane cell was designed to allow high fluid velocity parallel to the membrane surface as shown in Figure 2. The effective membrane area in the membrane cell was 19.63 cm². The permeate pressure was controlled by a vacuum controller (Model VC-30S, Okano Works, Ltd, Japan) at 1 Torr with an accuracy of ± 0.1 Torr. The permeate pressure was detected by a pressure sensor (Datametrics®, Model 1450, Edwards, MA). The permeate was condensed in a cold trap by liquid nitrogen. The condensed permeate in the cold trap was warmed up to ambient temperature to weigh and to measure its composition by an HP GC 5891 Series II equipped with an FID detector and a packed column. The column contains Carbowax 20M.

RESULTS AND DISCUSSION

Permeation of Pure Permeant Through PVA Membrane with Uniform Crosslinking Structure

Some basic but important parameters can be reliably obtained by separately studying the permeation of each pure component, avoiding too many parameters to be elucidated at the quantitatively level in the case of the permeation of the multicomponent mixture. Therefore, the permeations of pure water and acetic acid through membranes with different crosslinking density have been performed to study how significant an effect the crosslinking structure in the membranes can have on the concentration and ac-

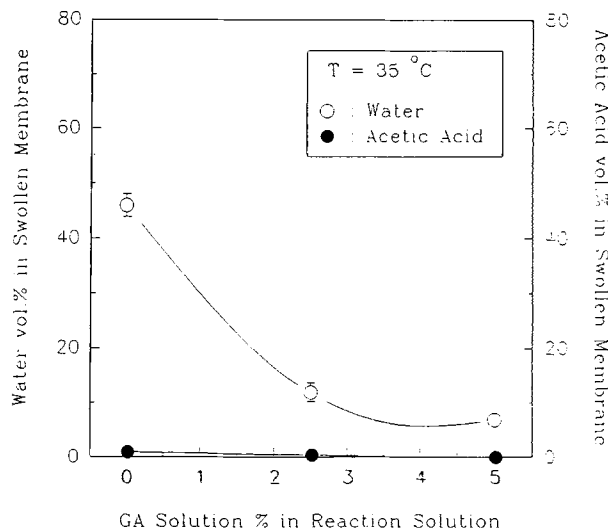


Figure 3 Water and acetic acid vol % in swollen membrane with GA solution vol % in reaction solution at 35°C.

tivity profiles of permeants and permeation properties.

Usually, as crosslinking density in a membrane increases, the membrane has a more compact network structure and less chain mobility. So, the amount of solvent absorbed in the membrane decreases and the free volume in it decreases as well. It reveals that the solubility of the liquid declines and the diffusivity, which is governed by the free volume, decreases due to the rigidity of the polymer chains in the membrane. This results in the permeation rate through the membrane to decrease, from the viewpoint of the solution-diffusion mechanism by which the pervaporation process is explained.

In this study, the swelling property of a membrane was used as a measure of the extent of crosslinking. Swelling measurements were carried out in pure water and pure acetic acid on the PVA membranes fabricated in different crosslinking agent content in the reaction solution. The result is shown in Figure 3. All measurements were repeated four or five times and the resulting data had a standard deviation of $\pm 7\%$. The swollen membranes were observed to be able to absorb much more water than acetic acid, showing a good affinity to water. Both water and acetic acid contents in the swollen membranes decreased with increasing crosslinking agent content in the reaction solution from 0 to 5 vol %, as a result of an increase in crosslinking density in the membranes. In our previous article,¹⁴ this observation was confirmed through both IR spectroscopy and a swelling test, and the solubilities of these two liquids

in the membrane were found to increase again with crosslinking agent content higher than 5 vol % due to the remarkable formation of aldehyde groups pending on the PVA chain.

The temperature dependence of the permeation rate can be expressed by an Arrhenius type of relationship¹⁰ in which a logarithmic form of flux is proportional to the inverse temperature. The Arrhenius plots of pure water flux through the cross-linked PVA membranes are presented in Figure 4 and show a good linearity in the given temperature range. However, the permeation rate of pure acetic acid was too small to collect in the cold trap. Each permeation activation energy, E_p , was determined from the slope of each plot, respectively, and plotted against the crosslinking agent content in the reaction solution in Figure 5. The permeation activation energy tends to increase with the crosslinking agent content, i.e., the crosslinking density. Since flux through a membrane is determined by both the solubility and diffusivity of a permeant, the E_p value should be dependent on both the diffusive activation energy, E_d , in the diffusion step and the heat of sorption, ΔH , in the sorption step:

$$E_p = \Delta H + E_d \quad (3)$$

In the pervaporation process, if there is a significant change in the membrane structure by the crosslinking reaction, the heat of sorption and the activation energy of diffusion will be changed, resulting from the changing solubility and the mobility of chain

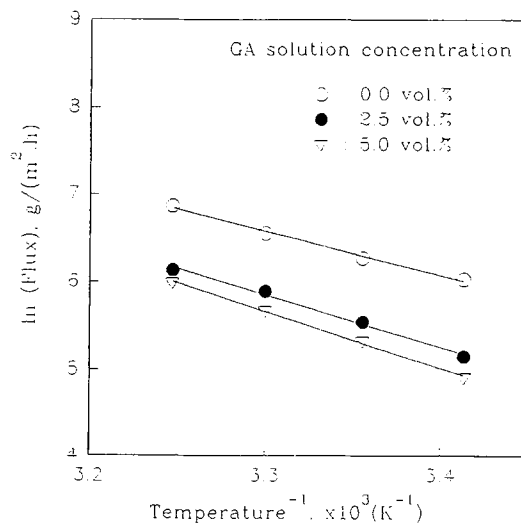


Figure 4 Arrhenius plot of water flux through membrane crosslinked at different crosslinking agent content in reaction solution.

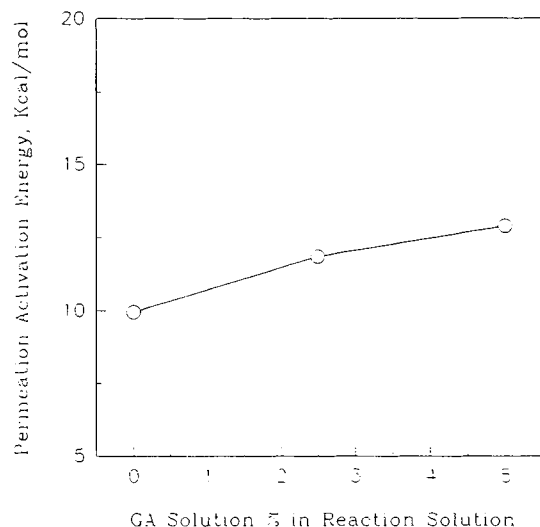


Figure 5 Plot of permeation activation energy of water with crosslinking agent content in reaction solution.

segments, respectively, so that an analysis of the permeation activation energy with crosslinking agent content can provide some clues on permeation behavior. Interaction between permeant molecules is thought to be a positive factor to the E_p because associate molecules having a large diffusing size require more energy for permeation than do isolated molecules, while the plasticization action of permeants influences negatively the E_p because it makes the polymeric chain segments more flexible.¹⁰ In the permeation of a pure liquid, the plasticization action of permeants is more likely to play an important role for the E_p value rather than will the interaction effect between permeants, which will play an important role in the permeation of the liquid mixture. Thus, more crosslinks make the membrane more rigid and compact, thereby increasing the energy required for diffusive transport through the membrane to decrease the diffusivity of the permeant and increasing the energy for the sorption of the permeant into the membrane to decrease the solubility of the

permeant. That is why the E_p value increases with crosslinking.

In the permeation of a pure component, its diffusivity, $D(C)$, in the membrane material is commonly represented by a two-parameter function accounting for its concentration dependence^{15,16}:

$$D(C) = D_0 \exp(\gamma C) \quad (4)$$

where D_0 is the diffusivity of the permeant in the membrane at zero concentration; γ , the plasticizing coefficient expressing the influence of the plasticizing action of the liquid permeant on the segmental motions of the polymeric membrane; and C , the permeant concentration in the membrane. These two parameters could be determined from nonlinear regression through fitting the Fick's diffusion equation including eq. (4) to experimental pervaporation and swelling data at various temperatures. The determined parameters and diffusion coefficient of water at the upstream-side surface of the membrane are presented Table I. As crosslinking density increased, the diffusion coefficient of water decreased, as explained previously, and the plasticizing coefficient decreased also because of reducing the plasticization action of water on the membrane.

Combining the above equation with the Fick's first equation and integrating over whole membrane thickness using the boundary condition, the expression of the permeant concentration profile at the steady state can be given as follows:

$$x = \frac{\exp(\gamma C_{m1}) - \exp[\gamma C(x)]}{\exp(\gamma C_{m1}) - 1} \quad (5)$$

where x is a relative distance from membrane surface at the feed side; C_{m1} , the concentration of the permeant absorbed into the membrane surface at the upstream side; and $C(x)$, the permeant concentration in the membrane at relative distance x . Indeed, examination of the representative function $C(x)$ shows

Table I Determined Parameters and Diffusion Coefficients of Water at the Upstream-side Surface of Membranes at 35°C

Parameters	GA Solution Vol % in Reaction Solution		
	0.0	2.5	5.0
γ	8.574	4.866	1.728
D_0 (m ² /s)	2.037×10^{-12}	4.269×10^{-11}	5.906×10^{-11}
D (m ² /s)	1.047×10^{-10}	6.972×10^{-11}	6.778×10^{-11}

that this profile tends to be convex if γ is greater than 1 and that the higher the values of γ the more pronounced the profile curvature. In fact, the activity gradient of a permeant is used as the driving force in the pervaporation process with sufficiently low permeate pressure. The relationship between the concentration and activity of the permeant can be expressed by Flory-Huggins thermodynamics¹³:

$$\chi = -\frac{\ln v + (1 - v_{m1})}{(1 - v_{m1})^2} \quad (6)$$

$$\ln a(x) = \ln v(x) + 1 - v(x) + \chi[1 - v(x)] \quad (7)$$

where v_{m1} and $v(x)$, are volume fractions corresponding to C_{m1} and $C(x)$, respectively; χ , the interaction parameter between membrane the material and the permeant; and $a(x)$, the activity of the permeant. Using eqs. (5)–(7), the concentration and activity profiles of water in the membrane could be simulated as shown in Figures 6 and 7, respectively. When the crosslinking agent content is higher in the reaction solution, these two profiles in the resulting membrane were less convex due to the plasticization action of water reduced by the formation of a more crosslinked structure in the membrane. Especially, there is a tremendous difference in the shape of the profiles between membranes treated with and without a reaction solution. Therefore, the profiles could be easily changed by the extent of crosslinking in the membrane. The parameters and

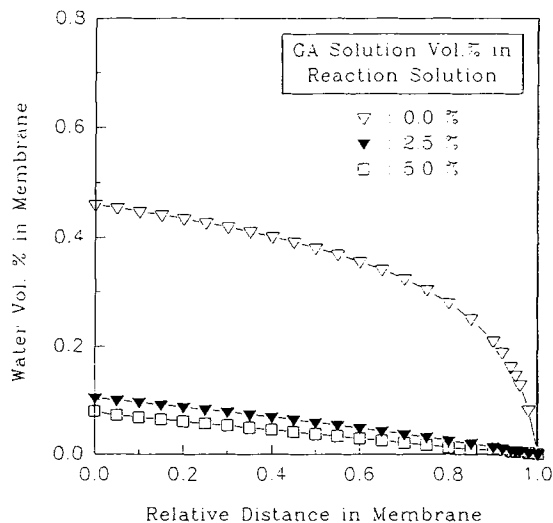


Figure 6 Water-concentration profile in membrane crosslinked at different crosslinking agent content in reaction solution.

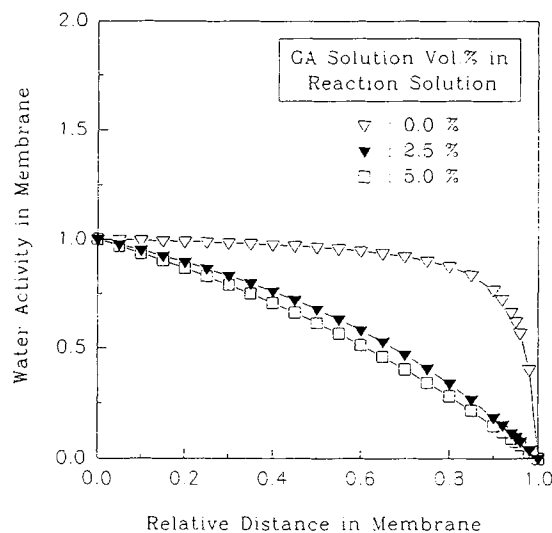


Figure 7 Water activity profile in membrane crosslinked at different crosslinking agent content in reaction solution.

profiles determined would be used to analyze qualitatively the permeation behavior of a water-acetic acid mixture through membranes with a different crosslinking gradient structure.

Permeation of Water-Acetic Acid Mixture Through Membrane with Crosslinking Gradient Structure

When a base membrane with one surface adhering to a polyester film was put into the reaction solution, the crosslinking gradient would be developed in the membrane because the crosslinking agent molecules in the membrane could be moved from the contacting surface to the other end of membrane only by diffusion. The extent of the crosslinking gradient was controlled by adjusting the exposing time, i.e., reaction time to reaction solution. The pervaporation separation of the water-acetic acid mixture was performed on the membranes fabricated with various reaction times. The results are exhibited in Figures 8 and 9. The membrane performance was found to be quite dependent on which membrane surface was in contact with the feed mixture, i.e., FHL (feed in contact with the membrane surface having a high crosslinking density) or FLH (feed in contact with the membrane surface having a low crosslinking density). In the case of loading the membrane in the FHL direction, in the early stage, the flux decreased rapidly with the reaction time and then decreased slowly until 30 min and, after then, almost leveled off or slightly decreased, while the separation factor

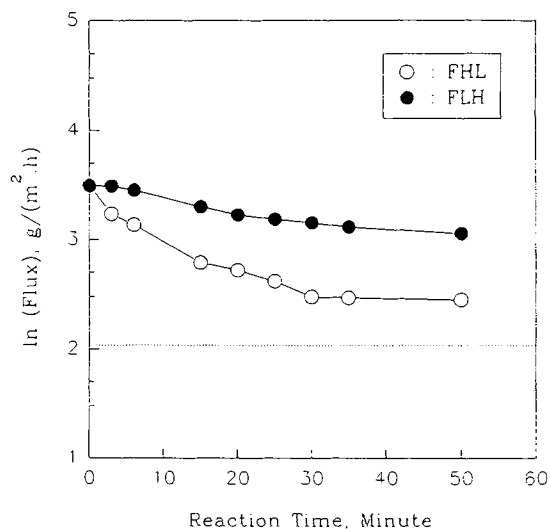


Figure 8 Plot of total flux vs. reaction time: feed composition = 70 wt % acetic acid and operating temperature = 35°C.

increased constantly. The reason for the flux curve with reaction time might be that once the crosslinking takes place at the membrane surface layer the crosslinking density in the layer increases with 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 diffusion. On the other hand, when the membrane was loaded in the FLH direction, it was very interesting to note that the flux showed a slight decrease with reaction time while the separation factor was not changed, was almost constant for the first 30 min of reaction time, and then started to increase with reaction time. From these observations, all the membranes appear to have a crosslinking gradient structure to a different extent and it can be postulated that it may take more than 30 min for the crosslinking agent molecules to move to the opposite end. Based on the parameters and profiles determined in the previous section, a schematic representation of possible concentration and activity of the permeant in the membrane at different crosslinking gradients is given Figure 10. 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 equation:

$$\begin{aligned}
 JL &= \int_0^{C_{m1}} D(C) dC \\
 &= D_{ave} C_{m1}
 \end{aligned}
 \quad (8)$$

where J is a flux; L , the membrane thickness; $D(C)$, the concentration-dependent diffusivity of a permeant; C , the concentration of the permeant in the membrane; 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. In eq. (8), flux is proportional to the product of the average diffusivity and solubility of the permeant in the membrane. In Figure 10, on the membrane surface exposed to the reaction solution, the water content in the equilibrium swelling, i.e., C_{m1} , decreases with reaction time because the crosslinking density increases, while on the other side surface blocked by the polyester film, C_{m1} is not changed so much because no or few crosslinking agent molecules reach the surface and the resulting crosslinking density is very low in the given reaction time. As a result, in FHL loading, the membrane having a longer reaction time will have lower C_{m1} and D_{ave} of the permeant and, in turn, the flux through the membrane must be larger according to eq. (8), but in FLH loading, C_{m1} and D_{ave} are slightly decreased with reaction time in the given reaction time range, so that the resulting flux cannot be decreased so much as in FHL loading. The dotted lines in Figures 8 and 9 represent the flux and separation factor of the membrane with a uniform crosslinking structure fabricated in the same reaction solution. The fact that the level-off value in FHL loading could not approach the dotted line in Figure 8 can be evidence for a nonuniform membrane structure attributable to the difficulty in diffusing crosslinking

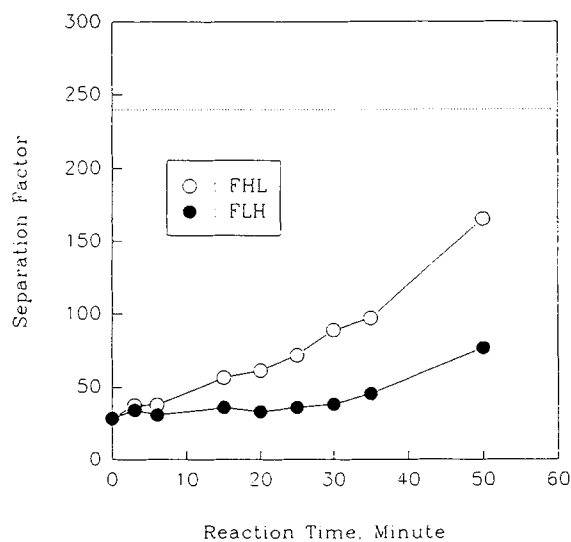


Figure 9 Plot of separation factor vs. reaction time: feed composition = 70 wt % acetic acid and operating temperature = 35°C.

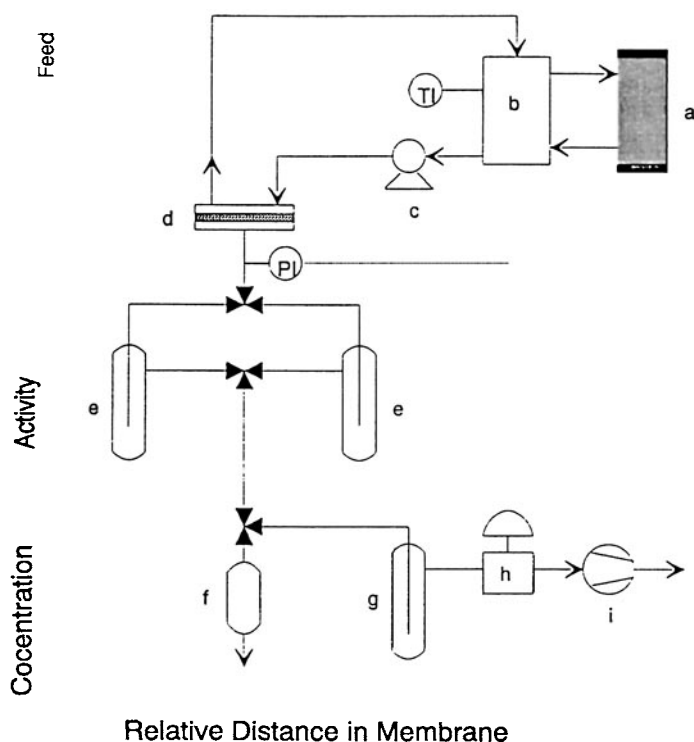
agent molecules through the rigid and compact surface layer which is exposed to the reaction solution.

The validity of the membranes having a crosslinking gradient structure proposed in this study is to achieve the enhancement of flux without reducing the membrane thickness. Even though the improvement of selectivity in the separation of the liquid mixture could not be obtained in this study, it is also thought to be possible to improve the selectivity of the membrane by using this technique if the concentration or activity of each permeant of the mixture can be controlled by appropriately adjusting the crosslinking gradient in the membrane because a difference in the concentration profiles of each component in the membrane may give rise to the separation of a liquid mixture.

CONCLUSIONS

Two types of PVA membranes crosslinked with glutaraldehyde (GA) were prepared by the solution technique where acetone was used as a reaction medium instead of aqueous salt solutions. The membrane having a higher crosslinking density had a lower plasticizing coefficient and a higher permeation activation energy due to the reduced plasticization action of the permeant. The concentration and activity profiles of permeants in the membrane were determined by the diffusion equation and the Flory-Huggins thermodynamics and the curves of the profiles tended to be more convex for the membrane with a low crosslinking density.

PVA membranes having a crosslinking gradient structure across the membrane thickness were prepared by exposing only one side of the base PVA membrane to the reaction solution while the other side was blocked by a polyester film to prevent the reaction solution from contacting. The extent of the gradient was controlled by the exposing time, i.e., reaction time. When the membrane surface having a high crosslinking density was in contact with the feed mixture (FHL loading), in the early stage, the flux decreased rapidly with increasing reaction time until 30 min and then almost leveled off or slightly increased while the separation factor increased constantly. The level-off value was higher than the flux of a uniformly crosslinked membrane due to a non-uniform membrane structure resulting from the difficulty in diffusing the crosslinking agent molecules through the rigid and compact surface layer which was exposed to the reaction solution. When the membrane surface having a low crosslinking density



- (a) FHL : feed facing with membrane surface having high crosslinking density
 (b) FLH : feed facing with membrane surface having low crosslinking density

Figure 10 Schematic representation of possible concentration and activity profiles of permeant in membrane with crosslinking gradient.

was in contact with the feed mixture (FLH loading), the flux and separation factor were not changed as much as in FHL loading because few crosslinking agent molecules reached across the thickness at this surface within the given reaction time, so that the permeant content at this surface, C_{m1} , and the average diffusivity of permeant, D_{ave} , could not change so much. Using the membrane having a crosslinking gradient, the enhancement of flux could be achieved without reducing the membrane thickness.

LIST OF SYMBOLS

Symbol	Units
$a(x)$	local permeant activity in membrane

C	permeant concentration in membrane	kg/m^3
C_{m1}	permeant concentration in membrane	kg/m^3
$C(X)$	local permeant concentration in membrane	kg/m^3
D_0	permeant diffusivity in membrane at zero concentration	m^2/s
$D(C)$	concentration dependent diffusivity in membrane	m^2/s
D_{ave}	average diffusivity in membrane	m^2/s
E_d	diffusion activation energy	kcal/mol
E_p	permeation activation energy	kcal/mol
J	permeation rate	$\text{g}/(\text{m}^2\text{h})$
ΔH	heat of sorption	kcal/mol
l	swollen membrane length	m
l_0	dry membrane length	m
L	membrane thickness	m
R	ideal gas constant	
t	reaction time	s
v	permeant volume fraction in membrane	
v_{m1}	permeant volume fraction at feed side surface of membrane	
x	relative distance from feed side surface of membrane	
γ	plasticizing coefficient	
χ	interaction parameter between permeant and membrane	

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