Characterization of Relaxation Phenomena and Permeation Behaviors in Sodium Alginate Membrane During Pervaporation Separation of Ethanol–Water Mixture

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SYNOPSIS

The pervaporation separation of a concentrated ethanol–water mixture with 90 wt % of ethanol content through a sodium alginate (SA) membrane was carried out to investigate both the relaxation process and permeation behavior of the membrane in pervaporation. From the swelling measurement of the membrane in 90 wt % of ethanol content of the aqueous solution, it was observed that SA has an excellent permselectivity toward water and a high solubility of water: about 1000 of sorption selectivity and 21 wt % of water content in the swollen membrane at 40°C. Its excellent sorption properties could result in the outstanding pervaporation performance for the aqueous solution; higher than 10,000 of separation factors and 120–290 g/(m² h) of fluxes, depending on the operating temperature. However, a serious flux decline took place with operating time due to the occurrence of a significant relaxation process in SA. The flux decline was remarkable at the beginning stage and then mitigated with operating time. The fluxes were reduced by about 40–50% because of the relaxation process during the measurement. To analyze these phenomena in more detail, the hysteresis behavior of membrane performance along with an operation temperature cycle was investigated. During the heating process in the cycle, the relaxation process was important to affect membrane performance while the formation of excess stress in the membrane might be a crucial factor during the cooling process. It was postulated from the experimental observations that in the heating process an increase in flux with temperature is restricted by a more rapid relaxation process at a higher operation temperature, while in the cooling process, the excess stresses in the membrane are formed and accumulated in and near the transition zone and near the area in the membrane because of slower relaxational consolidation in unequilibrium cooling than in relaxational dilation in the heating process, resulting in flux more sensitive to temperature than in the heating process. These phenomena were found diminished as the relaxation time increased with aging time. The relaxation phenomena were discussed through an analysis on permeation activation energy data obtained from the pervaporation experiments. A qualitative model was established to describe the relaxational phenomena in the membrane material during the pervaporation process by using the basic principles of polymeric relaxation and the experimental observations obtained in this study. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The pervaporation separation process has been focused on as an attractive technique for the separation of liquid mixtures. Extensive research has been made in finding the optimal membrane material that has special interactions with a specific component in a mixture to maximize performance like selectivity, flux, and stability.[1] It is well known that hydrophilic polymers are selected as a membrane material for the dehydration from various solvents because the water molecule is easily incorporated into the

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hydrophilic polymeric membrane. According to the solution–diffusion mechanism, separation in the pervaporation process takes place in two steps: selective sorption of liquid molecules into the membrane surface on the feed side and selective diffusion of them through the membrane due to differences in both of the solubilities and diffusivities of permeating constituents, respectively. From these points of view, natural high polymers, polysaccharides, are worth considering as a membrane material for dehydration. They possess good affinity toward water molecules as shown in several studies[2-6] dealing with the dehydration of alcohols through polysaccharide membranes. The cellophane membrane[2] and generated cellulose membrane[3] are reported to show a good selectivity in the dehydration of a water/alcohol mixture. Chitosan membrane,[4] one of the cationic polysaccharide membranes, also yielded high selectivity when its amino group was neutralized by polybasic acids or when it was crosslinked using H_2SO_4.[5] Among the polysaccharide membranes, alginate membranes are reported to present the most outstanding membrane performances for the dehydration of ethanol–water mixtures. Mochizuki et al.[6] showed that as alginic acid, one of anionic polysaccharides, was converted to alginate through neutralization by various bases the separation factor dramatically increased from 15 to more than 10,000 and the ethanol flux decreased from 0.85 to 2×10^{-4} kg/(m^2 h), while the water flux slightly decreased but still kept a high value, 200–900 g/(m^2 h), in the pervaporation separation of 90 wt % ethanol content of the ethanol/water mixture at 60°C. These phenomena were explained by an increase in the affinity of the membrane toward water by the neutralization and the contraction of "holes" (free volume) which was caused by the conformation change of the polysaccharide on the neutralization.

Membrane performance in pervaporation 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. When a rubbery state of the polymer is cooled, its molecular mobility decreases. At the glass transition temperature, T_g, the structural changes needed to maintain equilibrium cannot occur in the time scale of cooling and, instead, stress is created in the material which becomes a thermodynamically unstable glass. Since glass is not in a state of thermodynamic equilibrium, its physical and mechanical properties change with time as the material attempts to achieve equilibrium

through changes in its molecular configuration which can induce the release of the formed stress.[7-10] In the relaxation process, equilibrium is approached asymptotically. At aging temperatures near the T_g, equilibrium is reached within the time scale of the experiments: the higher the aging temperature, the shorter the aging time for equilibrium. This relaxation process can make the membrane structure denser by the configurational rearrangement of polymeric chains so that flux can be decreased with operating time, correspondingly.[11] It has been reported for gas separation that when further sorption or/and consolidation occurs in the membrane by changing the operation conditions during the process, conditioning (history), which is basically the result of the relaxation process, has an effect on sorption behaviors[7,12-15] and permeabilities[12] of permeants and, finally, may affect the membrane performance. In the pervaporation process, where a glassy polymeric membrane is employed for the dehydration of an aqueous mixture, a pronounced anisotropic swelling is developed in the membrane, by which the phase gradient can be established across the membrane thickness from the rubbery state at the feed-side membrane surface to the glassy state at the permeate-side surface. The sorption behavior in the glassy region near the permeate-side membrane surface may be similar to the sorption behaviors of organic vapors or condensable gases in glassy membranes for gas separation. In this case, relaxation phenomena will be complicated by different membrane mobility with the location in the membrane since the relaxation process can progress, depending on the mobility of the polymer material. Unfortunately, so far, no research has yet been made on the relaxation in the pervaporation process.

In this study, to characterize the relaxation process and the permeation behavior of the sodium alginate membrane in a dehydration process, the swelling measurement of the membrane in a 90 wt % ethanol content of an ethanol/water solution was carried out with an equipment which is designed to precisely measure both the concentration of an absorbed liquid in the membrane and the swelling ratio of the membrane, and pervaporation separations of the ethanol/water mixture through the membrane were performed under an isothermal operation at 50°C as well as under a dynamic operation along with a temperature cycle having a temperature range of 40–80°C. The relaxational phenomena in the membrane during the pervaporation will also be elucidated through an analysis on the experimental data of membrane performance measured in both the isothermal and dynamic operations. A qualita-

tive model will be suggested to explain the relaxation behavior in the glassy membrane, using the basic principles of polymer relaxation and experimental observations.

EXPERIMENTAL

Materials

Sodium alginate (extrapure grade) was purchased from Showa Chemical Inc. (Japan). Ethanol (guaranteed reagent) was supplied by Merck (Germany). Ultrapure deionized water was used. All chemicals were used without any further purification.

Membrane Preparation

A sodium alginate (SA) casting solution, 2.5 wt %, was prepared by dissolving SA in water. The casting solution was cast onto a glass plate 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. The resulting membrane thicknesses were 11–13 μm for the pervaporation test and 32 μm for the swelling measurement.

X-ray Diffractometer

To investigate if crystallization takes place significantly during pervaporation, wide-angle X-ray scattering was performed using an X-ray diffractometer (Model D/MAX IIIB, Rigaku) with a scintillation counter detector using CuK$_\alpha$ radiation as a source. Angles (2θ) used ranged from 2° to 50°. All samples were films with thicknesses of 11–13 μm.

Measurements of Swelling Ratio and Preferential Sorption

In an isotropic material, since a change in 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

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

where L_x, L_y, and L_z are the dimensions of the swollen membrane in x, y, and z directions, respectively, and subscript o denotes the dry membrane. Therefore, the volume fraction of the solvent in the swollen membrane can be expressed in the following form[16]:

$$\phi = \frac{R_L^3 - 1}{R_L^3} \left(= \frac{L_x L_y L_z - L_{xo} L_{yo} L_{zo}}{L_x L_y L_z} \right) \qquad (2)$$

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 aqueous solutions for 2 days for an equilibrium swelling. For the measurement of preferential sorption, the swollen slabs were taken out of the solution after equilibrium swelling, wiped off with tissue paper as quickly as possible, and then were placed into the glass tube X which, subsequently, was fitted to the device as shown Figure 1. While the glass tube was heated up 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), and two packed columns. Each sample injector was actuated by compressed air. The columns were 5 ft long with $\frac{1}{8}$ 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 a carrier. For the measurement of the swelling ratio, the swollen slab was taken out and
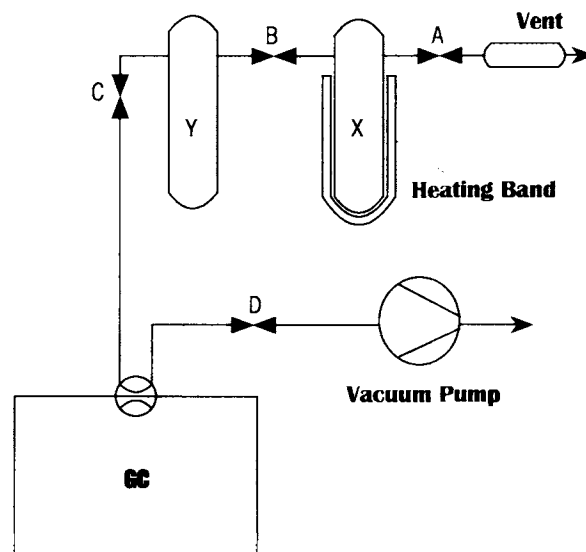

Figure 1   Schematic representation of desorption apparatus.

put on a paper wetted by 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 [eq. (2)]. Each measurement of preferential sorption and swelling ratio was repeated three to five times.

Pervaporation

A 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 a membrane surface. The cell structure is depicted elsewhere.[17] 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 the heating tape to heat the feed mixture. The feed mixture temperature was controlled by a temperature controller (Cole-Parmer Instrument Co., Digi-Sense®, Chicago, IL) and the permeate pressure was controlled by a PID controller (Okano Works Ltd., Vacuum Controller VC-30S, Osaka, Japan). The composition of the permeate vapor was determined by an on-line gas chromatography (GC) analysis. The GC 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 up 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 component in the feed and permeate, respectively.

To investigate the flux change with operating time, pervaporation was performed with a feed mixture of 90 wt % ethanol content at 50°C for a whole day. After 1 day of the pervaporation experiment, the membrane used was maintained in the membrane cell with the permeate side vented to the atmosphere overnight (14 h) and then the same per-
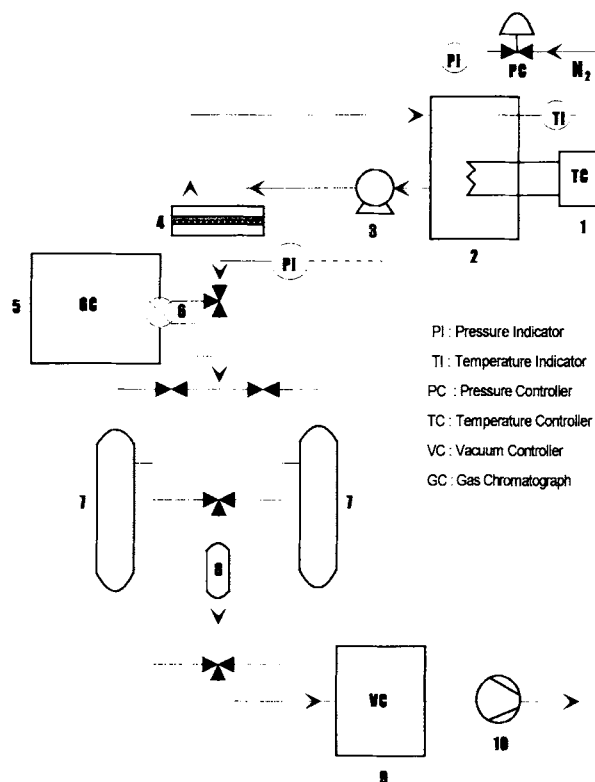
Figure 2 Schematic representation of pervaporation apparatus: (1) temperature controller; (2) feed tank; (3) pump; (4) membrane cell; (5) gas chromatograph; (6) sample injector; (7) cold traps; (8) vent to atmosphere; (9) vacuum controller; (10) vacuum pump.

PI : Pressure Indicator
TI : Temperature Indicator
PC : Pressure Controller
TC : Temperature Controller
VC : Vacuum Controller
GC : Gas Chromatograph

vaporation experiment was carried out again the next day. The pervaporation experiment was continued for 6 days with the same membrane. To elucidate the hysteretic behavior on membrane performance, the feed temperature was controlled along with a temperature cycle where the temperature was increased from 40 to 80°C in a sequence of temperature steps in the heating process, and then the same procedure was repeated from 80 to 40°C in the cooling process. The measurements of flux and the separation factor were made every 10°C in each process: After the measurement of membrane performance at a certain temperature step, the feed mixture was cooled or heated to next temperature step with a certain rate in the cooling or heating process, respectively, and then after reaching the new temperature, the feed mixture was applied to isothermal pervaporation experiment and the sample under a steady-state operation could be collected 2 h later when the isothermal process was started. After the experiment in each process (heating or cooling), the membrane was kept in the membrane cell at room temperature as described in the isothermal experi-

Table I Comparison of Preferential Sorption Data of Sodium Alginate (SA) with Other Membranes in 90 wt % Ethanol Content of Ethanol/Water Mixture

Membrane	Temperature (°C)	Absorbed Liquid in Membrane			Ref.
		Ethanol Content (wt %)	Solubility (wt %)	Sorption Selectivity α_{sorp}	
SA	40	0.89	21	1002	This study
Modified PVA[a]	45	60.9	4	5.8	14
PVA(GFT)[b]	60	60.3	12	5.9	20

[a] Modified PVA: poly(vinyl alcohol) crosslinked with amic acid.

[b] PVA(GFT): GFT poly(vinyl alcohol) membrane.

ments, so that all the experiments could be carried out with the same membrane. The heating and cooling rates employed were 1–0.7 and 0.8–0.6°C/min, respectively. The temperature cycle was continuously repeated three times. The permeate pressures for all the experiments were kept below 0.4 mmHg.

RESULTS AND DISCUSSION

Swelling Measurement

Membrane permeability is a function of solubility times diffusivity of the permeants in a membrane phase under a particular condition of pervaporation. In binary component pervaporation, the preferential sorption of one component over the other amounts to a sorption selectivity, to be compared with the selectivity of distribution systems. The sorption selectivity, α_{sorp}, can be determined by

$$\alpha_{sorp} = \frac{x_{water}/x_{ethanol}}{X_{water}/X_{ethanol}} \quad (4)$$

where x and X are the weight fractions of each component in the liquid absorbed in the membrane and in the feed, respectively. The sorption selectivity may or may not be identical to pervaporation selectivity, any departure being indicative of a contribution of diffusion selectivity α_{diff} to the overall separation. Thus, the separation factor, α, given in eq. (3) can be rewritten as follows:

$$\alpha = \alpha_{sorp}\alpha_{diff} \quad (5)$$

Sodium alginate (SA) or alginic acid sodium salt, which is neutralized by NaOH, is a gelling polysaccharide extracted from giant brown seaweed. SA was insoluble in ethanol and in ethanol/water solutions in which the alcohol content was more than 70 wt

%. Below 70 wt % ethanol content, a significant weight loss by slow extraction was observed during the swelling test. Thus, SA could be used for the dehydration of concentrated alcohol without any modification to improve the material stability. The results of the swelling measurement of SA in 90 wt % of ethanol content at 40°C are presented in Table I compared with those of other hydrophilic membrane materials. In comparison, poly(vinyl alcohol), which is one of the typical hydrophilic materials well known for good affinity toward water, had water solubilities of 4–12 wt % and sorption selectivities of about 6, but SA showed much higher values for both water solubility and sorption selectivity. It reveals that SA possesses a very high affinity to water and can be expected to have an excellent permselectivity toward water in pervaporation owing to the preferential sorption of water.

Membrane Performance with Operating Time and Temperature Cycle

All the membranes used in this study were prepared in the same batch to make sure identical thermal histories are imposed on them before measuring membrane performances. Fluxes and separation factors at 50°C are plotted with six consecutive sets of operating time in Figures 3 and 4, respectively. After each set of measurements, the membrane was kept in membrane cell with the permeate side open to atmosphere for 14 h, which will be called "aging" hereafter. On the whole, the membrane showed an excellent membrane performance. Especially, the pervaporation separation factors were very high, ranging from 20,000 to 30,000, which had already been expected from the fact that the membrane has a high preferential sorption of water as discussed in the previous section. As will be discussed again later, the separation factor in this study was found not to change very much with temperature. In this case,
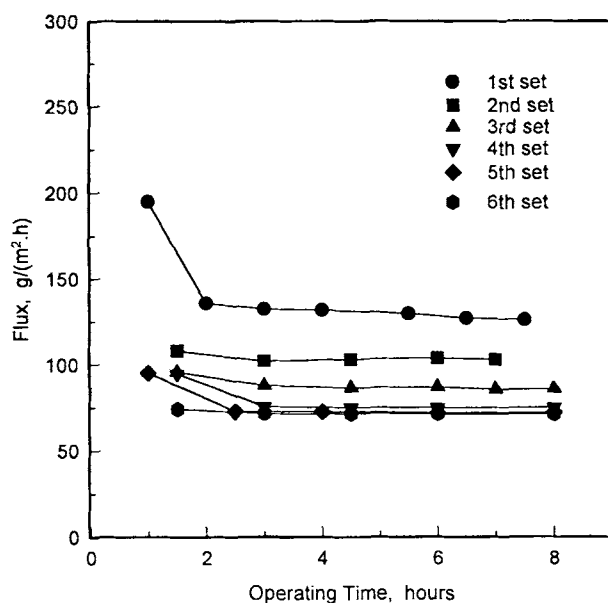
Figure 3 Plots of flux through SA membrane against operating time at 50°C and 90 wt % ethanol content in feed with various aging times.

Figure 4 Plots of separation factor through SA membrane against operating time at 50°C with various aging times.

from eq. (5), diffusion selectivity could be calculated as 20–30, which is very small compared to sorption selectivity of 1000. These observations can confirm that the excellent separation performance must be attributed mainly to the highly selective sorption in this system.

The effects of operating time and aging can be observed on membrane performance from the flux data. The first set of experiments was conducted with an unrelaxed membrane which had not experienced any aging process. The resulting flux decreased dramatically with operating time in the beginning state and then decreased slightly. After going through the first aging, the second set of fluxes were measured to be lower by 40–50%. As the aging was repeated, the subsequent flux decreased less and leveled off from the fourth set of experiments (Fig. 5), and the change of flux with operating time became less significant while the separation factor was not changed very much, as shown in Figure 4. The possible causes of the decrease of flux with operating time and aging can be a change in the feed composition and the occurrence of crystallization, and the relaxation process during the six sets of experiments. The ethanol content of the feed mixture was kept almost constant, changing from 89.89 to 90.08 wt % during the experiments. From the results of wide-angle X-ray diffractometry, no evidence for the occurrence of any significant crystallization during the experiments could be found, as presented in Figure
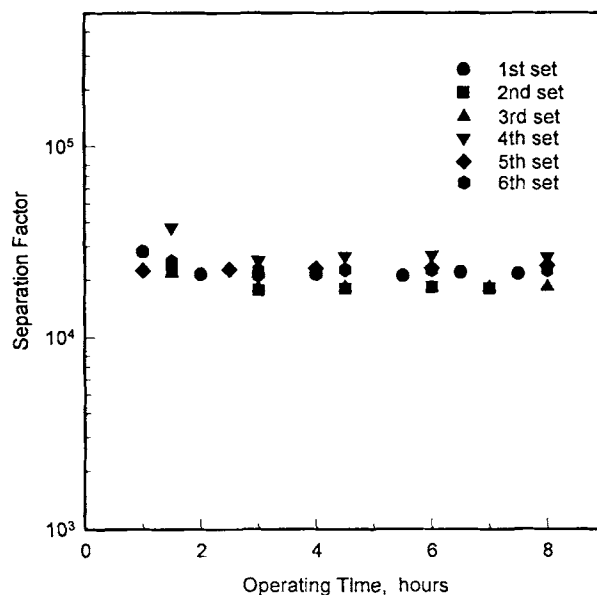
6. Thus, the effects of the change of feed composition and crystallization during the experiments could be negligible in this study. As a result, it could be concluded that the drop of flux after aging and the slight decrease of flux with operating time must be the result of the relaxation process occurring during aging and the pervaporation process, respectively. The relaxation process is a configurational change of polymeric chains taking place only in glassy mate-
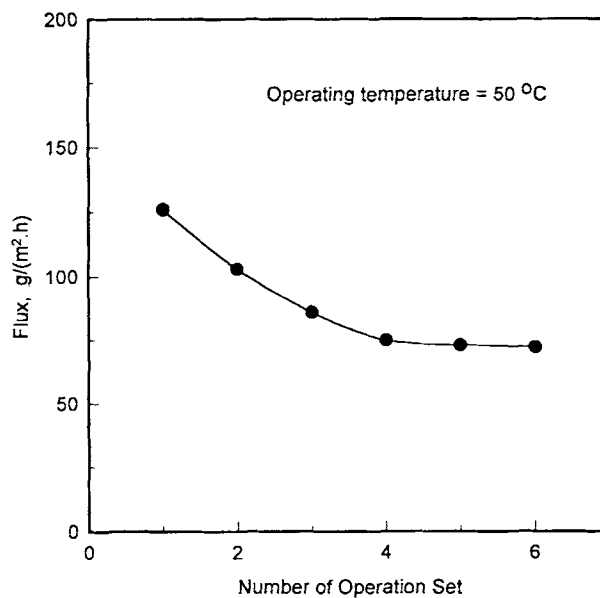
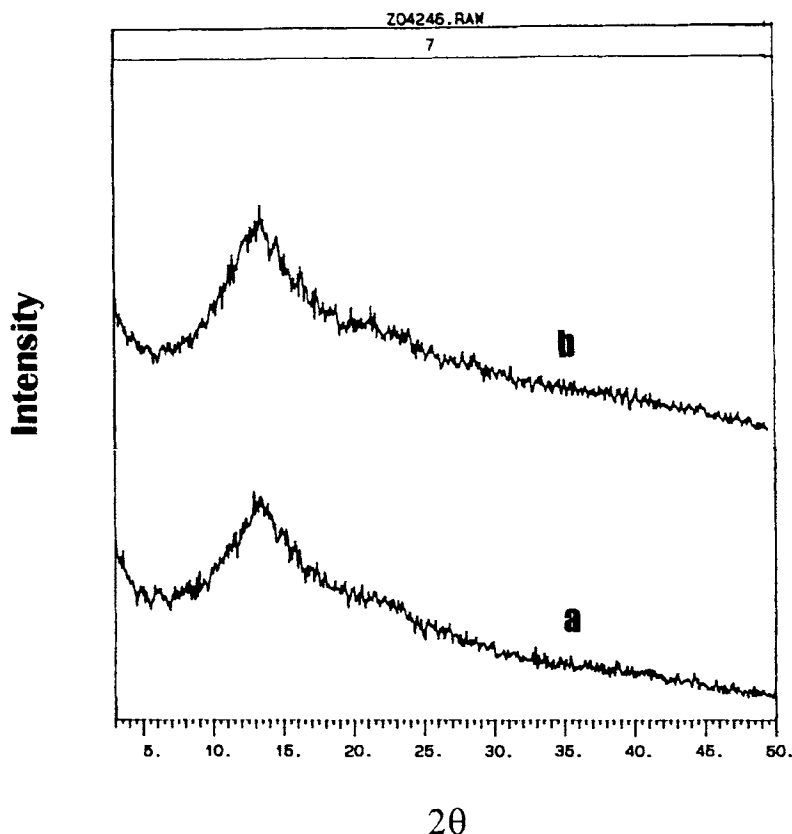**Figure 5** Flux change with aging time at 50°C.

Figure 6   X-ray diffractograms of SA membranes before and after 6 days of pervaporation operation: (a) after 6 days of operation; (b) before operation.

rial. In pervaporation, the permeate pressure was kept well below the saturated vapor pressure of permeants so that the membrane surface at the permeate side in this study could be in a glassy state, whereas the membrane surface at the feed could be swollen by sorbed liquid molecules and, thereby, it could be in a rubbery state. Therefore, it can be expected that the relaxation may occur in a transition region between the rubbery and glassy state and/or near the membrane surface at the permeate side.

The reason why the decrease of flux was much more drastic after the aging than with the operating time is presumably due to the higher permeant concentration in the membrane during the aging process. Since the permeate side in the membrane cell was exposed to the atmosphere in the aging process, the permeant concentration on the membrane surface at the permeate side should be higher than that at the permeate pressure near the vacuum, depending on the diffusion rate of the permeant molecules from a membrane surface at the feed side, so that the permeant concentration profile could become broader to increase the total permeant concentration in the membrane. More permeants in the membrane

can enhance polymeric chain mobility to accelerate or facilitate the relaxation process. That is why the membrane after the aging went through the dramatic decline of the flux. It was reported[9,10] that as the relaxation process progresses or aging time increases the relaxation time becomes longer due to the densification of the material by rearrangement of the polymer chains. Finally, a point might be reached at which the relaxation proceeds too slow for the time scale of measurement. In this case, the flux would not be changed significantly with operating time as presented beyond the fourth set of experiments. More details on the relaxation process will be discussed with a qualitative model for describing the relaxation behavior in a membrane during the pervaporation process later.

Table II shows changes in the flux and separation factor with operating temperature in each cycle, which were executed sequently. To easily determine the tendency of the changes, the results of the first two cycles in the table are plotted in Figures 7 and 8, but those of the third cycle could not be plotted because of a too little change of the membrane performances to distinguish themselves

from the others. Almost all the separation factors were determined to be higher than 10,000. From these figures, the following phenomena were observed which might be particular enough to be worthy of notice:

- In a temperature cycle, the flux measured at a certain temperature in the heating process was higher than that measured in the cooling process at the same temperature, and as the cycle was repeated, the fluxes got closer to each other, i.e., the difference in the fluxes decreases.

- The aging process caused the flux to increase or decrease, depending on which process proceeded prior to the aging: Aging after the heating process decreased the flux while that after the cooling process increased the flux.

These phenomena of interest can be explained in association with different relaxation behaviors in the cooling and heating processes. A cycle of operation involves heating, aging, cooling, and aging processes in that order. The heating or cooling process consists of consecutive temperature steps of 10°C and isothermal operations for a certain time period at each step. The aging procedure was already described before. The heating, cooling, aging, and isothermal operation at each step could be considered as a kind of relaxation process. There may be three factors which can affect membrane mobility in a cycle of operation: temperature, plasticization action of sorbed permeant molecules, and relaxation. When the temperature is high, the polymeric material can have more flexible polymeric chains. The sorbed permeant molecules in the sorption step plasticize
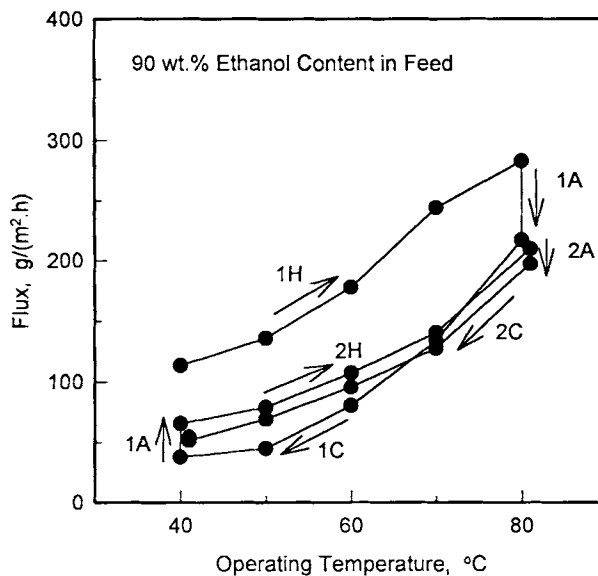

Figure 7 Hysteretic changes of fluxes through SA membrane with operating temperature cycles at 90 wt % ethanol content in feed: 1H and 2H = heating process in the first and second cycles, 1C and 2C = cooling in the first and second cycles, and 1A and 2A = agings in the first and second cycles, respectively.

the membrane material and enhance its mobility. The relaxation process can make the glassy membrane denser by densification through a configurational rearrangement of the polymeric chains. From the viewpoint of their basic principles,[9,15] these three factors could be postulated to mutually affect each other in a complicating way: An increase in temperature can cause not only an increase in the solubility of the permeant in the membrane but also

Table II   Membrane Performance with Operating Temperature of Each Temperature Cycle in Pervaporation Separation of 90 wt % Ethanol Content of Feed Composition

| | Temperature (°C) | 1st Cycle | | 2nd Cycle | | 3rd Cycle | |
		Heating (1st day)	Cooling (2nd day)	Heating (3rd day)	Cooling (4th day)	Heating (5th day)	Cooling (6th day)
Flux [g/(m²h)]	40	113.5	27.7	65.7	51.8	54.3	53.3
		135.8	44.9	79.1	69.3	70.0	74.3
	60	177.9	80.6	107.3	95.7	92.7	101.5
	70	244.2	134.0	140.6	127.7	122.4	136.3
	80	272.3	217.3	209.7	197.3	179.9	179.4
Separation factor	40	7,670	27,264	13,226	38,001	21,942	25,541
	50	18,548	31,350	44,991	37,648	31,681	26,318
	60	27,099	22,950	47,863	34,342	22,380	24,039
	70	32,718	23,068	107,130	48,640	26,307	23,914
	80	34,740	24,784	72,572	53,883	33,953	24,541
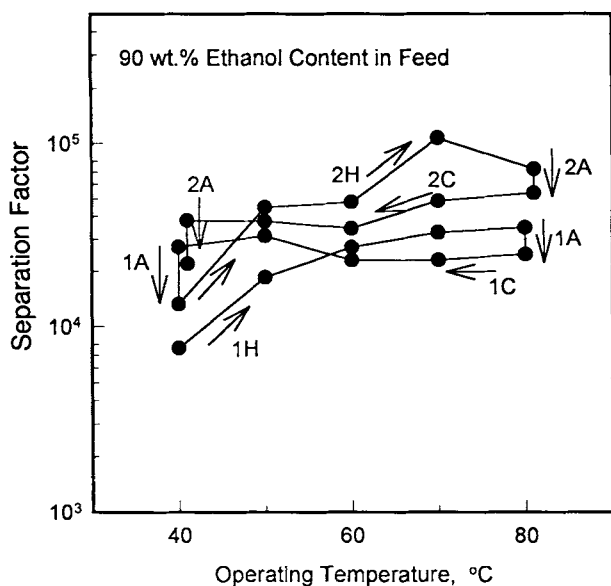
Figure 8 Hysteretic changes of separation factors with operating temperature cycles: 1H and 2H = heating process in the first and second cycles, 1C and 2C = cooling in the first and second cycles, and 1A and 2A = agings in the first and second cycles, respectively.

faster relaxation; highly sorbed permeants facilitate the relaxation process; and the relaxation process may have an effect on the solubility of permeants in glassy state of material although the process is very slow in nature. Therefore, it is difficult to elucidate the effect of each factor separately due to the complicated relationship between them.

The experiment in the first cycle was carried out with an unrelaxed membrane. In the first cycle, as the feed was heated, the membrane mobility could be increased not only by the effect of temperature but also by the increased plasticization action of the sorbed permeants, and the relaxation might occur more rapidly under such a membrane mobility. Hence, increase of the temperature and the relaxation process can affect the flux in opposite ways: The increase of temperature increases flux while the relaxation decreases flux due to the formation of a dense membrane structure. Therefore, increase of flux with temperature would lessen because of a more significant relaxation process at higher temperature. In a subsequent aging process after the heating process, since permeant concentration in the membrane increases with time and membrane flexibility could increase correspondingly, further remarkable relaxation could be imposed on the membrane. That is why the flux after the aging process was decreased. In a consequent cooling process, when the feed was cooled from step to step during pervaporation, the

membrane could be consolidated commensurate with decreasing membrane mobility which might be attributed to both the decrease of temperature and concomitant decrease in the permeant concentration in the membrane. In fact, it is not clear why the flux is more sensitive to temperature in the cooling than in the heating process, but it might be explained in terms of different relaxation rates in the cooling and heating process rates as follows: It has been reported[13] that the plasticization effect of absorbed permeants in the sorption step is more pronounced than in desorption. In a cycle operation, heating and cooling processes are analogous to the sorption step and desorption, respectively, in light of that heating (or cooling) of the feed can increase (or decrease) the permeant concentration in the membrane. Due to the smaller plasticization effect for the cooling process, relaxational consolidation in the cooling process would be even slower than the relaxational dilation occurring in the heating process and, thus, the transition zone in the membrane and near the membrane surface at the permeate side membrane might be consolidated less at a temperature in unequilibrium cooling, similarly to polymer material which is vitrified earlier in more rapid cooling.

The less relaxation or consolidation to the new circumstance causes an excess stress to more strain the membrane matrix. The stress may make the polymer chains strained or rigid, resulting in reducing the diffusivity or flux of the permeant through the strained medium, compared with that through the membrane subjected to only the temperature effect. As the membrane is cooled down further, the excess stress may be accumulated so that the flux can be more reduced. In a subsequent aging process after the cooling process, the accumulated stresses will be released by the relaxation, by which the reduced flux could be restored to some extent. However, the flux was not restored completely to the original value due to the progress of the irreversible relaxation process. It is summarized that during a temperature cycle of operation that in the subsequent processes of heating and aging the relaxation process progresses appreciably and it makes the flux decrease, while in the subsequent cooling process, the excess stresses created by slow consolidation relaxation in unequilibrium cooling, which resulted in depression of the flux, was released by the relaxation during the following aging and, thereby, the reduced flux can be restored to some extent. As the cycle was repeated, the relaxation progresses further and the relaxation time increases as much. The relaxation process slows down with the aging time and, finally, a point could be reached at which the relax-

ation is too slow for the experimental time scale. After the point, fluxes become closer to each other in heating and cooling processes.

Figure 9 shows the Arrhenius plots of fluxes with temperature at different heating cycles. The plots have a good linearity in the given range of temperature. The permeation activation energies of each process were determined from the slope of the plots and are presented with the operation day in Figure 10. An analysis on the permeation activation energy can provide a good frame to interpret the relaxation behavior. Since the flux through a membrane in the "solution–diffusion" mechanism is determined by both the solubility and diffusivity of the permeants, the permeation activation energy should depend on both the activation energy for the diffusion and the heat of sorption. The swollen membrane surface at the feed was rubbery throughout all the experiments, which could be characterized by high equilibrium sorption even at the lowest temperature in this study as described in Table I. Therefore, the permeant concentration at the membrane surface or the heat of sorption must always be identical at a certain temperature regardless of the relaxation process and, herein, the permeation activation energy change with the relaxation is thought to be associated with a change in the diffusion property of permeants. In Figure 10, the permeation activation energy in the heating process seems to stem from an increase in the energy required for the diffusive jump of per-
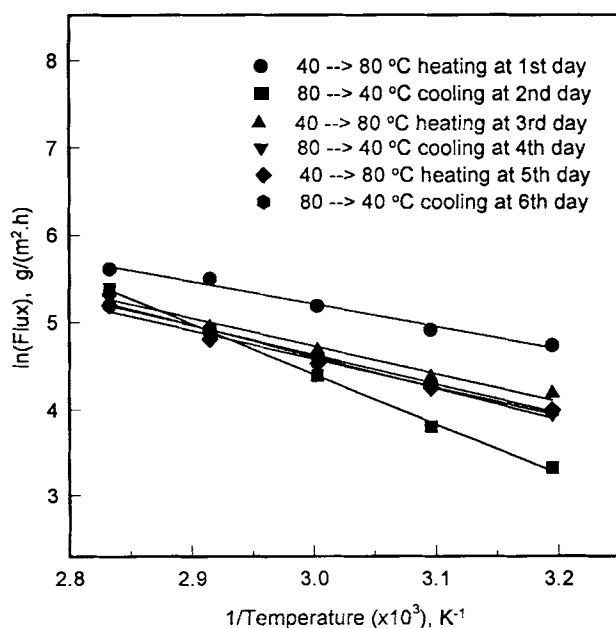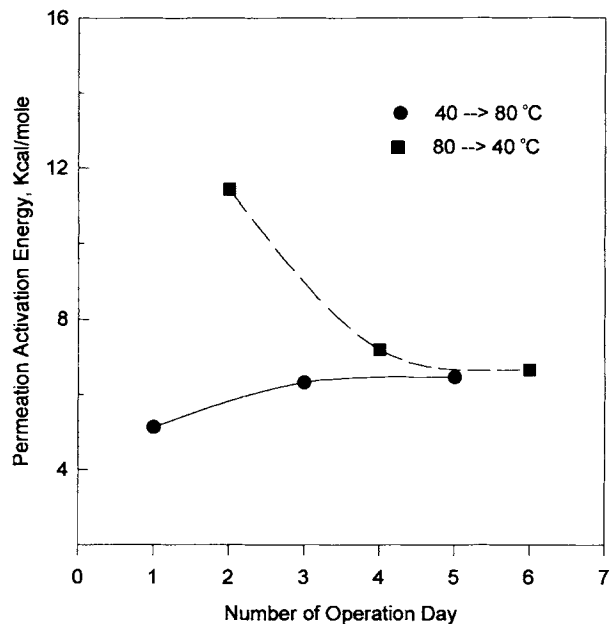

Figure 10 Permeation activation energies with aging time calculated from Figure 9.

meants because of decreasing membrane mobility in the relaxation process while a decrease in the permeation activation in the cooling process results from a decrease in energy for the diffusive jump of permeants due to releasing the excess stresses in the relaxation process. The figure also shows that the activation energy in the cooling process is much higher than that in the heating process at the beginning stage. The formation of the excess stresses in the cooling process due to a slow consolidation relaxation could be responsible for the higher permeation activation energy in the cooling process as discussed before. As the relaxation progressed, the activation energies in both processes came closer each other. The results supports the validity of the postulations made on the analysis of membrane performance data.

Figure 11 illustrates the plots of fluxes against the operation day which includes both operating time and aging time. In the beginning, the flux in the cooling process is lower than that in the heating process and the difference between them decreases with increasing temperature, and both curves become closer to each other with the operation day as discussed above. The reason for that was explained by that the relaxation rate tends to be fast in the beginning stage, and then with time, the rate decreases rapidly to zero where the relaxation time is too long for the experimental time scale, and with increasing temperature, the membrane mobility is higher so that the membrane can undergo a greater
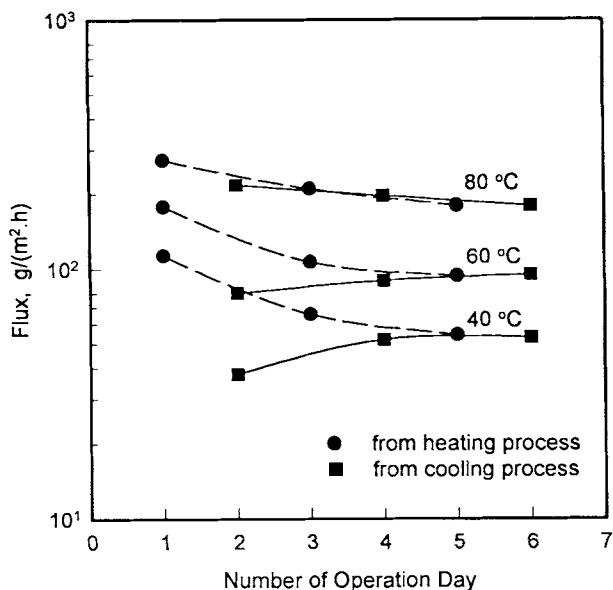

Figure 9   Arrhenius plots of fluxes with operating time with different aging times.

Figure 11   Flux changes with day or cycle of operation at different temperatures.

that at the permeate side. In the pervaporation process, the solubility of a permeant in a membrane is maximum at the feed-side surface and then decreases across the membrane thickness to zero at the permeate-side membrane surface under a permeate pressure well below its saturated vapor pressure, showing the concentration profile of the permeant, i.e., anisotropic swelling in the membrane. The concentration profile of a target component is dependent on both the affinity of the permeant toward the membrane material and the plasticization actions of other permeants as well as the target permeant on the membrane material for the permeation of the permeant. More permeants absorbed in the membrane exerts more plasticization action on the
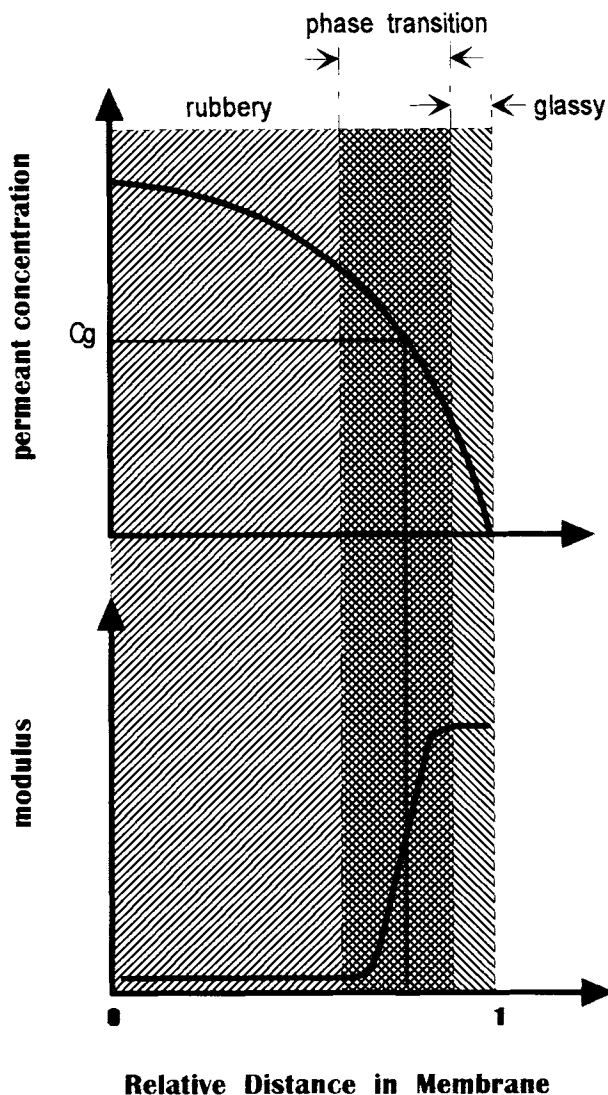
extent of relaxation in the beginning stage before measuring and then be subjected to a slower relaxation regime, resulting in a smaller extent of relaxation progressing over most of the measuring time. Thus, fluxes measured in both processes were slightly changed with the operation day at the highest temperature, 80°C, and were almost superposed into one curve.

Qualitative Model for the Relaxational Behavior of Glassy Membrane in Pervaporation

In the following sections, we will suggest a qualitative model that can explain the relaxational behavior of a glassy membrane in pervaporation, using the basic principles of polymer relaxation and experimental observations in this study.

Isothermal Pervaporation Process

Liquid sorption by a glassy polymer often changes the material from glassy to rubbery. The sorbed liquid molecules plasticizes the polymer matrix, depresses the T_g, and brings about the glass transition at temperatures below the T_g of the dry polymer. Figure 12 presents schematically the typical profiles of the permeant concentration and corresponding modulus developed in a glassy membrane during a steady-state process at a certain temperature. The relative distance in the membrane indicates a normalized position in the membrane, with 0 referring to a membrane surface at the feed side, and 1, to

Relative Distance in Membrane

Figure 12   Schematic profiles of permeant concentration and bulk modulus in glassy membrane during pervaporation: Cg, glass transition concentration.

polymeric chain mobility, resulting in that the T_g value of the polymer is reduced passing through the operating temperature and, thereby, the glassy polymer can become rubbery.[15] Therefore, the membrane structure in the pervaporation process may range from the rubbery state at the feed-side surface to the glassy state at the permeate side surface, i.e., the membrane will have a phase-state gradient across the membrane thickness.

In this case, there must be a region having a state corresponding to the phase transition between the glassy and rubbery states at the operating temperature in the membrane. Herein, there is a permeant concentration called the "glass transition concentration" at which the operating temperature equals the glass transition temperature. Centering around this region, the phase state of the membrane is divided into a rubbery state in the thickness region directed to the feed side and a glassy state in the region directed to the permeate side. Looking at the modulus curve, the modulus of the glassy state is so high that the polymer segments would lose their flexibility due to the freezing of the side-group motions and relaxation time is approximately infinite while the rubbery state has a low modulus or a high enough mobility to be in equilibrium where the relaxation time is almost zero. Also, in the rubbery region, the crystallization process is very likely to proceed for a crystalline polymeric membrane during pervaporation since crystallization generally takes place at temperatures between its T_g and melting point.

Figure 12 also depicts that the modulus in both the rubbery and glassy regions are constant. In fact, the modulus has a change commensurate with the change of the permeant concentration in the zones, but the modulus change is very negligible, compared with the change in the transition zone. In and near the transition zone, a practical relaxation process occurs in the time scale of the experiment to a different extent with the position in the membrane because of the different local permeant concentration or different local membrane mobility: The glass transition temperature, relaxation time, and thermodynamical unstability increase going to the permeate side. A more swollen part can get through a more rapid relaxation because of more flexible polymeric chains and vice versa. Thus, it is expected that stress can presumably be developed in the transition region due to the nonuniformity in the properties with position. When the relaxation progresses significantly in the transition region, the segmental mobility of the polymeric chains becomes decreased and the corresponding modulus increased so that

the transition curve may be shifted to the rubbery zone. As a result, the glassy zone can be extended as much as can the rubbery zone be narrowed, which comes out as a manifestation of a decrease in the flux. In addition, the amount of absorbed permeants also determines the position of the transition zone in the membrane: With decreasing the amount, the transition zone drifts to the feed-side surface and then, finally, the resulting membrane is in the glassy state all across the membrane thickness, the phase gradient disappearing. On the other hand, generally, rubbery materials are often selected for the removal process of organic components from aqueous solutions. A permeant concentration profile may be developed in the membrane as in the dehydration process, but the phase gradient cannot be created across the membrane because the membrane material is always rubbery at the operating temperature irrespective of the permeant concentration in it.

Dynamic Pervaporation Process Along with a Temperature Cycle

When absorbed molecules significantly plasticize the glassy polymer during the sorption process, the resulting polymer will undergo reduction of the relaxation time, depending on the amount of the absorbed permeant molecules.[7,12–14,18] This can cause the sorption behavior of the permeant molecules in the glassy membrane to be complicated by two significant factors: diffusion (Fickian) sorption and relaxation-controlled sorption. Fickian sorption sites are originally available in the dry virgin polymer while relaxational sorption sites are new sites created by the plasticization action of the sorbed permeant molecules and morphological alternations. Thus, the total sorption is composed of Fickian and relaxational sorptions. Since the creation of the new sorption sites by the morphological alternations is slow in nature, the diffusion equilibration may be approached before significant relaxation occurs. The plasticization action of permeant molecules on polymer chains is only present during the sorption experiment but not during desorption experiments at a vacuum. Thus, the dilation relaxation process in sorption will be considerably faster than is the consolidation relaxation in desorption. Wessling et al.[13] found in high-pressure dilation experiments with glassy aromatic polyimides in an isothermal process that as permeant concentration increases the fraction of the Fickian sorption decreases and the relaxation sorption increases due to the plasticization action of the permeant molecules on the

polymer chains and, in turn, lowering the relaxation time of the polymer.

Based on these facts, the following model for describing the sorption behavior in a glassy membrane exposed to an organic vapor subjected to heating or cooling can be established, a system which can be considered in association with the transition and glassy zone of glassy membrane developed in the pervaporation process. Since the solubility of a liquid in a polymer increases with temperature, the heating process is similar to the sorption or dilation process while the cooling process is a kind of desorption or consolidation process. In the heating process with integral temperature steps, the membrane is considered in which the permeant concentration in the membrane can increase from $C0$ to an equilibrium concentration $C1$ in a temperature step from $T0$ to $T1$, respectively. Now the situation is assumed to reach one where an equilibrium concentration $C1$ is already present in the polymer when the next temperature step from $T1$ to $T2$ is applied. A part of the sorption sites for the temperature step from $T1$ to $T2$ can be occupied by the polymer matrix relaxation in the temperature step from $T0$ to $T1$. The polymer matrix relaxation is attributed to the temperature effect as well as to the plasticizing effect of the sorbed permeant molecules on the polymer chains as mentioned before. These sites are Fickian sorption sites for the temperature step from $T1$ to $T2$. But since they are already occupied, the sites cannot contribute to the Fickian dilation fraction and the Fickian sorption in the case of polymer relaxation is smaller than in the ideal case of elastic reversible sorption. As a consequence, the ratio of relaxational sorption sites to Fickian sorption sites increases. Successive temperature steps result in a decreasing Fickian sorption site fraction with increasing fraction of relaxational sites because of an increasing temperature and the more significant plasticization action may reduce the relaxation time of the system. The contributions of these two sorptions to total sorption with temperature is schematically depicted in Figure 13. The Fickian part of sorption kinetics decreases with incrementally increasing temperature steps and the situation may occur where no Fickian sorption can be observed from a certain temperature above the T_g.

The proposed model can also account for the cooling process and here especially for the hysteretic behavior as shown in Figure 7. The observation to be discussed first is which sites the relaxational or Fickian sites will consolidate faster in the cooling process. On a molecular scale, Fickian sorption seems to be related to motions of shot parts of the
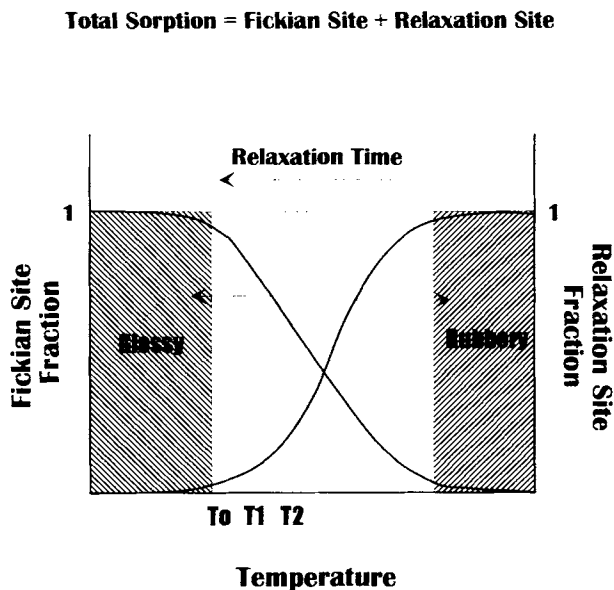
Total Sorption = Fickian Site + Relaxation Site

Figure 13 Equilibrium fractions of Fickian and relaxational sorptions of permeants with temperature in glassy membrane.

polymer chain; relaxational sorption is related to motions of long polymer chain segments. Thus, Fickian consolidation is obviously much faster than is relaxational consolidation. The relaxational sorption remains in the polymer, causing the consolidation isotherm to lie above the sorption isotherm. In other words, in the cooling process, consolidation occurs first in the fraction of Fickian sorption sites and then very slow consolidation is followed in the relaxational sorption sites as described in Figure 13. In addition, due to a smaller plasticization effect for a cooling process compared to a heating process, the consolidation relaxations can be even slower than the sorption relaxations. Consolidation relaxations can be so slow on the experimental time scale that residual dilation can be observed, depending on the cooling rate and isothermal operation time. The residual dilation also decreases with time through continuous relaxation, but it is unlikely that the polymer sample consolidates into its original volume.

Now, we can discuss the permeation behavior of permeants through a glassy membrane along with temperature cycle based in the principles suggested above. A schematic representation of the profiles of permeant concentration and the bulk modulus developed across the glassy membrane at different operating temperatures is shown in Figure 14. The concentration and modulus in this figure are assumed to be constant with time, i.e., the properties measured at infinite operation time, and the permeant concentration at the feed-side membrane
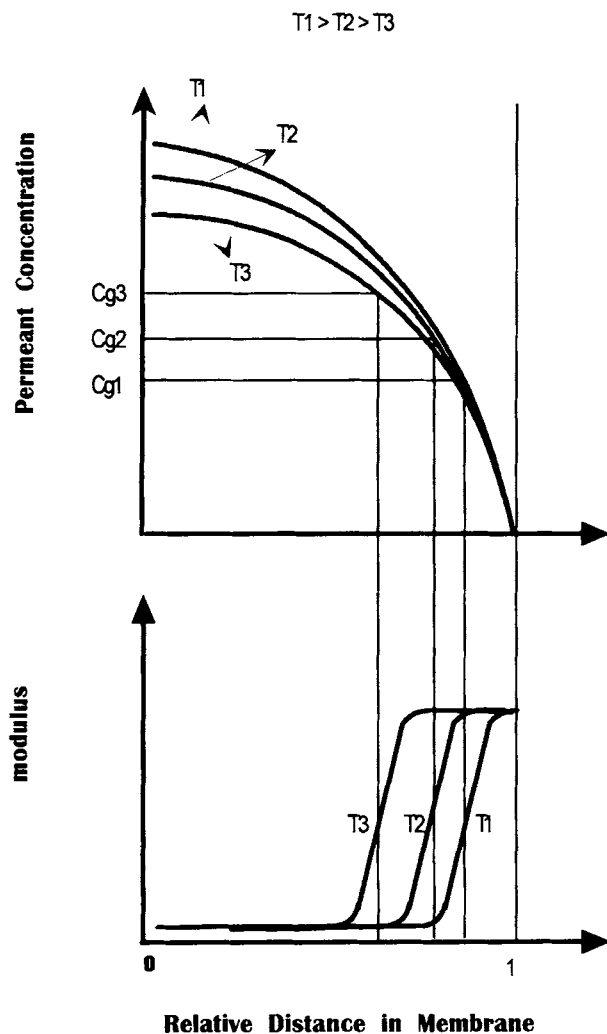
T1 > T2 > T3

Figure 14 Visualization of profiles of permeant concentration and bulk modulus in glassy membrane at different temperatures during pervaporation: Cg1, Cg2, and Cg3 are the glass transition concentrations at temperatures T1, T2, and T3 (T1 > T2 > T3), respectively.

surface is high enough for the membrane surface to be rubbery in the temperature range of the experiment. At lower temperature, the equilibrium permeant concentration in a membrane surface contacted with feed tends to be lower while that in a membrane surface with permeate is always zero at the permeate pressure near the vacuum condition. Often, the glass transition temperature is approximated by the isoviscosity or isomodulus characteristic in a given system.[19] Considering only the temperature effect, when temperature is low, the bulk modulus of the system is high at a certain permeant concentration because of lowering of the polymeric chain mobility. Thus, at lower temperature, more permeant molecules in the membrane are needed

for more plasticization action in order to maintain the same bulk modulus and the permeant concentration involved in the membrane should be higher, i.e., the glass transition concentration should be increased with decreasing temperature. As a consequence, the concentration profile and the corresponding modulus curve with operating temperature can are established in the membrane as shown in Figure 14. In the heating process from T3 to T1, the modulus curve may shift to the permeate side and the rubbery portion will be increased while the glassy portion will be decreased as much. Some of the stressed glassy region will be transformed into the rubbery state by the effects of temperature and the plasticization action of additional permeant molecules absorbed. However, the relaxation process proceeds more rapidly at higher temperature so that the relaxation sorption can become more significant, as can be seen in Figure 13. At the same time, the relaxation process can make the membrane denser by the rearrangement of polymeric chains, shifting the transition curve to the opposite direction of the temperature effect. It can be expected that the transition curve can be less shifted for the given temperature change because of the relaxation process, giving less increase in the flux with increasing temperature compared to the unrelaxed system. Aging after the heating process causes further relaxation to decrease the flux.

On the other hand, unequilibrium quenching or cooling of the feed mixture during pervaporation may bring about a pronounced reduction of the permeant concentration in the membrane which induces excess stresses in the material. It was mentioned that the Fickian consolidation proceeds faster than does the relaxation consolidation. Thus, in the cooling process from T1 to T2, the Fickian sorption sites will be consolidated first and then the relaxation sites will be very slowly consolidated with time, and the extent of consolidation achieved is less than that of dilation obtained in the heating process with the same temperature step from T2 to T1, because the relaxation consolidation is even slower than is the relaxation dilation due to less plasticization action of the sorbed permeants in the cooling process. Furthermore, the extent of the consolidation developed is related to the cooling rate. Since the cooling process is a sort of relaxation process where temperature changes continuously, the higher cooling rate can induce less relaxation consolidation, resulting from a shorter time scale of the process. Puleo and Paul[12] investigated that the permeability coefficient of the gas permeant through cellulose acetate is higher in the desorption or consolidation

process than in the dilation process and these phenomena were explained in terms of the formation of a less consolidated structure (or "more residual dilation") due to less relaxation consolidation in the desorption process. The resulting polymer in the consolidation process will have a more dilated structure containing a lesser amount of permeant molecules than in the dilation process.

Figure 15 illustrates a change in the permeant concentration profile during the cooling process from $T1$ to $T2$. The thick solid line for $T2$ indicates a permeant concentration obtained at an operation time much longer than the experimental time scale. In the rubbery state, the relaxation time is so small that the matrix can be thought to be in the equilibrium state in the time scale of the experiment. In the glassy region, the relaxation time is large to such an extent that only Fickian behavior can exist in both the dilation and consolidation processes in the time scale of the experiments. In and near the transition zone, going to the glassy zone, the contribution of Fickian behavior to the consolidation process becomes pronounced and the residual dilation will be decreased while, going to rubbery zone, the fraction of the relaxation consolidation increases but the relaxation time decreases so that the residual dilation can be decreased. Consequently, the residual dilation due to slow relaxation consolidation will be maximized in the middle of the transition zone in the time scale of the experiments. Since the dynamic permeability of permeants through the zone with more residual dilation is higher, the permeant concentration in the zone is smaller as shown in Figure 15, creating more residual stress. The reduction of permeant concentration will be accumulated through successive temperature steps in the cooling process and may induce the depression of flux by reducing both membrane mobility and the diffusion coefficient of the permeants. In aging after the cooling process, the residual dilation will decrease by further relaxational consolidation as a manifestation of stress relaxation and, then, the depressed permeant concentration will be recovered to some extent, depending on the aging time.

As the temperature cycle is repeated, the size distribution of free volumes is narrowed by a disappearing large size of free volumes[9] in and near the transition zone and the relaxation time increases, and, then, finally, a point can be reached at which the relaxation time is so large for the experimental time scale that the relaxation process cannot affect the dilation and consolidation processes in the operation along with the temperature cycle. Thus, the pervaporation process becomes reversible and the
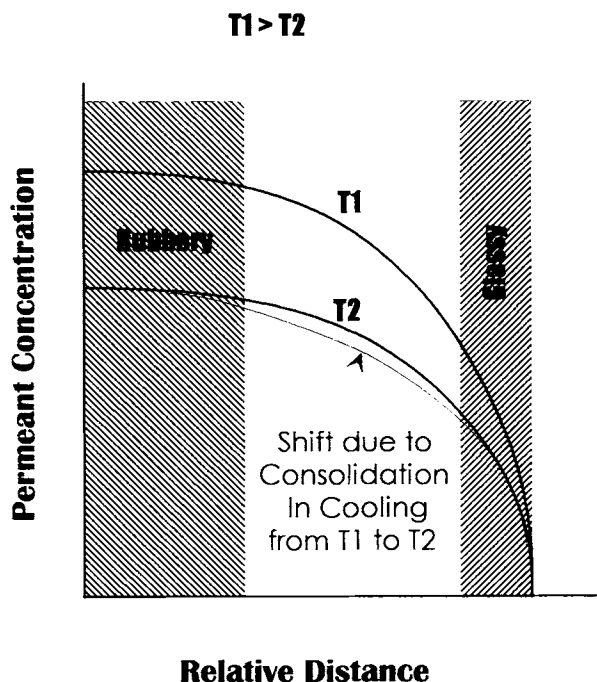

Relative Distance

Figure 15 Visualization of the shift of permeant concentration in membrane for decreasing temperature from T1 to T2 during pervaporation process.

permeation activation energies in both heating and cooling processes approach asymptotically to a value with repeating the temperature cycle.

CONCLUSIONS

The pervaporation separations of a concentrated ethanol–water mixture with 90 wt % of ethanol content through the SA membrane were performed to elucidate the relaxation behavior during the pervaporation process. The SA membrane showed an excellent membrane performance in the dehydration process: separation factors of higher than 10,000 and 120–290 g/(m² h). The outstanding separation ability of the SA membrane could be attributed mainly to a highly preferential sorption for water.

SA membranes in the pervaporation process were subjected to a significant relaxation process which caused a pronounced decline in the flux. In pervaporation with a temperature cycle, the relaxation process was appreciable during the consecutive processes of heating and aging, and it could make the polymeric chains rearrange to a denser structure which decreases the flux, while, during the subsequent processes of cooling and aging, the excess stresses created by a slow consolidation relaxation in unequilibrium cooling, which resulted in depres-

sion of the flux, were released by the relaxation in aging and, thereby, the reduced flux can be restored to some extent. The relaxation process was remarkable in the beginning stage and lessened and then leveled off with aging time. These phenomena were discussed using an analysis on the permeation activation energies obtained from the pervaporation experiments.

A qualitative model was established to explain the experimental phenomena, using the basic principles of polymer relaxation where Fickian and relaxation behaviors were competitively exerted on dilation or consolidation processes, depending on temperature and permeant concentration in the membrane.

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