

Pervaporative Permeations of Homologous Series of Alcohol Aqueous Mixtures through a Hydrophilic Membrane

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Received 28 October 1999; accepted 19 February 2000

ABSTRACT: The permeation behaviors of permeants were investigated in the pervaporation of a homologous series of alcohol aqueous mixtures through a hydrophilic poly(vinyl alcohol) (PVA). The PVA membrane was crosslinked with glutaraldehyde. A homologous series of alcohols used in this study were methanol, ethanol, 1-propanol, and 1-butanol. The pervaporation experiments were carried out with feed having 70–97 wt % of alcohol contents and at various feed temperatures. In a high alcohol content above 92 wt %, the permeation rate was increased in the order of the interaction strength between alcohol and water in the feed. However, in a low alcohol content below 90 wt %, the tendency of the permeation rate was found to be the opposite, indicating that the interactions between permeant constituents play an important role in determining the permeation and separation of the mixtures. These observations were discussed in terms of changes in the interaction between the permeant/permeant or the permeant/membrane in varying feed compositions and feed temperatures. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 703–713, 2001

Key words: pervaporation; hydrophilic membrane; poly(vinyl alcohol); interactions between permeant/permeant and permeant/membrane

INTRODUCTION

For binary mixtures, the coupling of fluxes has to be taken into account. The transport of each component of a binary mixture in a membrane can be determined by the local concentration of each component of the mixture. Thus, many investigators suggested that the diffusivity of each component is a function of the concentration related to the free volume, which, in turn, depends on the local composition in the ternary system: permeant *i*/permeant *j*/membrane.^{1–4}

The coupling of fluxes occur significantly in the permeations of polar/polar constituent mixtures, such as in alcohol/water mixtures. In this case, feed composition has a strong effect on the selectivity as well as the permeation rate. The order of magnitude of the selectivity is at the same time far lower than is the ratio of the permeation rates of pure components. This behavior is usually interpreted as a plasticizing effect of the permeants on the membrane. Therefore, a linear dependence of the permeant diffusivity is not suitable to take into account large plasticizing effects. Another cause of the coupling of fluxes is the interaction between permeant molecules, which means a positive or negative influence of the presence of one component on the rate of transfer of another. For the coupling of fluxes, it can be concluded that the

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Journal of Applied Polymer Science, Vol. 79, 703–713 (2001)
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presence of the permeant j affects the transport of permeant i in two ways⁵:

1. The plasticizing effect of the permeant on a polymeric membrane as a result of the interaction between the permeant and the membrane, generally increasing both the diffusivity and solubility of i .
2. The interaction effect, due to the remaining interaction between molecules i and molecules j in the polymer, which can increase or decrease the diffusivity of component i .

In addition, a factor also affecting the permeation behavior is the size of the permeant molecules or the permeating unit. Increasing the permeant size has a negative effect on the permeation through a membrane.

In this study, the permeation behavior of permeants in pervaporation of a homologous series of an alcohol aqueous mixture through a crosslinked poly(vinyl alcohol) (PVA) was examined. The PVA membrane was crosslinked with glutaraldehyde. The homologous series of alcohols used in this study consisted of methanol, ethanol, 1-propanol, and 1-butanol. The pervaporation experiments were carried out with feed having 70–97 wt % of alcohol contents and at various feed temperatures. This study concentrated on the comparison of the permeation behaviors of a homologous series of alcohol aqueous solutions. The sorption and permeation behaviors of the feed mixtures through the membrane are discussed in terms of both the plasticizing effect and interaction effect of the permeant molecules in the membrane.

EXPERIMENTAL

Materials

PVA was purchased from the Aldrich Chemical Co. (Milwaukee, WI). The average molecular weight and saponification of the PVA were 50,000 and 99%, respectively. Glutaraldehyde (GA) (25% content in water, extrapure grade), hydrochloric acid (HCl) (35% content, extrapure grade), and acetone (guaranteed reagent) were purchased from the Junsei Chemical Co. (Tokyo, Japan). Ultrapure deionized water was used. All chemicals were used without any further purification.

Membrane Preparation

A PVA solution was prepared by dissolving PVA in distilled water at about 80°C. The polymer content in the solution was 10 wt %. 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. For the preparation of a membrane with a uniform crosslinking structure, the dry membrane was peeled off the glass plate and immersed at 40°C for 48 h in a reaction solution which contained 10 vol % of GA and 0.05 vol % of HCl in acetone. 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. Details on the crosslinking reaction were described elsewhere.⁶ The membranes prepared ranged from 15 to 25 μm in thickness.

Swelling Measurements

Swelling measurements of the crosslinked membranes⁴ were performed to determine the amount of water absorbed in the membranes. Dry membrane strips were immersed in water thermostated at 30°C for 48 h to allow the strips to reach equilibrium sorption. The dimension of a strip was 7×1.5 cm. After measuring the swollen length, l , of a strip at equilibrium sorption, the strip was dried for 30 h at room temperature under a vacuum and then the dry length, l_0 was measured. The swelling ratio, R , for an isotropic material is defined as

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

All measurements were repeated four or five times and the resulting data had a standard deviation of $\pm 6\%$. The solubilities of water in the membranes were calculated from the swelling ratio.

Permeation Apparatus

A schematic pervaporation apparatus used in this study is illustrated in Figure 1. The apparatus used in this study was well described elsewhere.^{6–8} The feed tank having a capacity of 4 L is equipped with a heater and a cooler. The feed

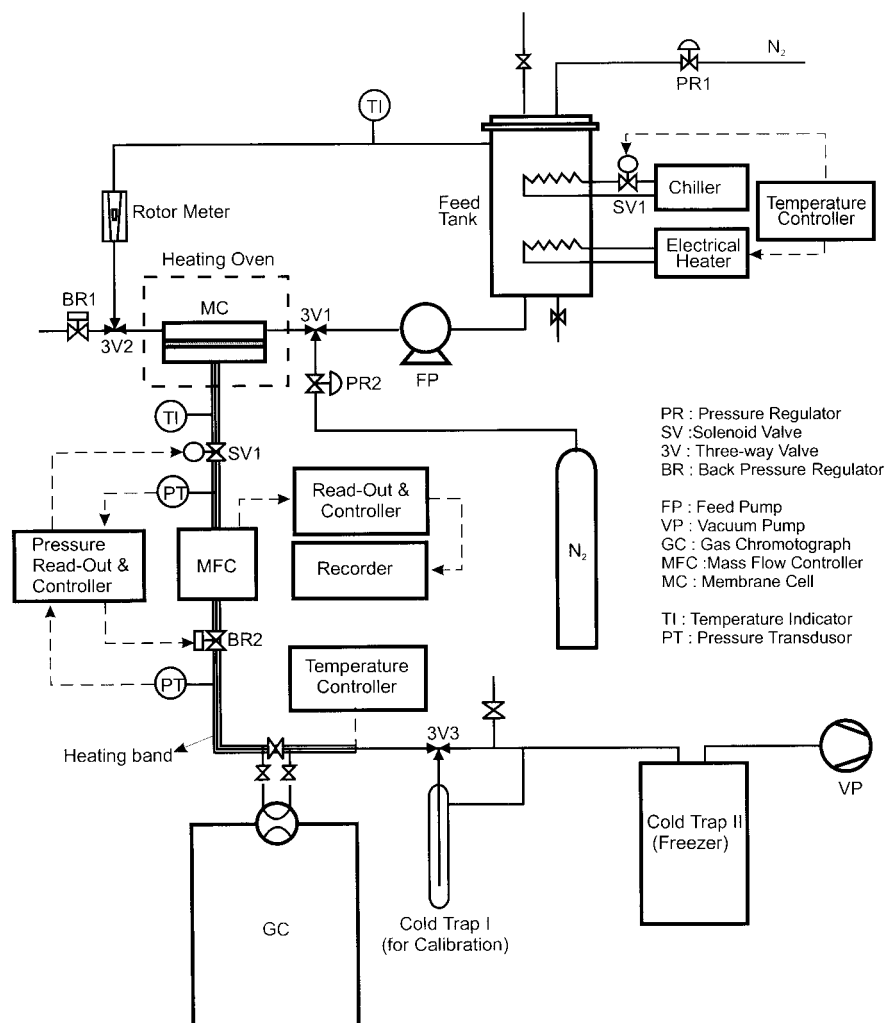


Figure 1 Schematic representation of pervaporation test apparatus.

was circulated from the feed tank through the membrane cell by a pump with an adjustment function of the flow rate. The membrane cell was placed in the heating oven to maintain the membrane cell at a desired temperature. The effective membrane area was 18.1 cm^2 . To dry the membrane in the membrane cell before measuring the permeation properties, the upstream space in the membrane cell was purged with nitrogen gas through a gas inlet valve and, at the same time, the downstream side was evacuated by a vacuum pump. The measuring system of permeation properties which is connected with the permeate side of the membrane cell consists of a mass flow meter (MFM) and a gas chromatograph (GC). The line in this system was wrapped with a heating band to control the temperature in it and thereby prevent the condensation of the permeate

vapor on the inner wall of the line. The permeate pressure was also controlled by the back-pressure regulator. A solenoid valve was installed between the membrane cell and the MFM and cut off the permeate line to protect the measuring system when an emergency situation, such as membrane breakage, occurs.

To minimize the pressure drop developed across the MFM (Brooks, Japan) during permeation, the pressure difference between the inlet and outlet of the MFM was adjusted to a low value of 4.5 psi so that permeate pressure could be maintained as low as possible in the downstream side of the membrane cell. The highly sensitive recorder (Model 7155B, Hewlett-Packard) was connected with the MFM to directly sense even a slight change of voltage produced by the instantaneous flux. The maximum sensitivity

of the recorder was 0.1 mV/cm, which is sensitive enough to detect the instantaneous flux in comparing it with the maximum voltage of 5 V produced in the MFM. Thus, the voltage produced in the MFM by flux was recorded with the operating time and then it was converted into the corresponding flux by a relationship between the produced voltage and flux. The relationship was made by correlating the amount of the permeate vapor collected in the cold trap I with the corresponding voltage produced in the MFM during a steady-state permeation. As a result, the measuring system could determine even a very small flux on-line.

The gas chromatographer (5890 Series II Plus HP GC) was equipped with an integrator (HP 3396 Series II), a sample injector (6-port valve) actuated by air, a TCD detector, and a packed column. The column was 6 ft long with $\frac{1}{8}$ -in. inside diameter having a Porapak Q. Thus, the permeate vapor can be injected directly into the column by the injector and thereby the composition of the permeate vapor is determined directly and accurately. The driving force for the system was provided by the vacuum pump and all permeate waste was collected in cold trap II (refrigerated cold trap, JeioTech Ltd, Seoul, South Korea). No liquid nitrogen was needed for determination of the flux except when the correlation curve between the voltage in the MFM and the resultant flux was established. In all measurements, permeate pressures were kept below 4 Torr. The separation factor of water was calculated by the following equation:

$$\beta = \frac{Y_{\text{water}}/Y_{\text{alcohol}}}{X_{\text{water}}/X_{\text{alcohol}}} \quad (2)$$

where X and Y are the weight fractions of the component in the feed and in the permeate, respectively.

RESULTS AND DISCUSSION

Swelling Measurements

The solubility parameters of water and the respective alcohols are presented in Table I. One of the approaches to describe the interaction between materials is the simple solubility parameter theory. The solubility parameters of materials can be used as a measure of interaction between them. The solubility parameters δ_t used in this

Table I Solubility Parameters of Methanol, Ethanol, 1-Propanol, 1-Butanol, and Water⁹

Permeant	$\delta/\text{MP}^{1/2}$			
	δ_d	δ_p	δ_h	δ_t
Methanol	15.1	12.3	22.3	29.6
Ethanol	15.8	8.8	19.4	26.5
1-Propanol	16.0	6.8	17.4	24.5
1-Butanol	16.0	5.7	15.8	23.1
Water	15.5	16.0	42.4	47.9

approach each have the following three components: δ_d , δ_p , and δ_h , separately quantifying the contribution of dispersion forces, polar forces, and hydrogen bonding to the solubility process, respectively. According to this theory, a good solvent for a polymer has a solubility parameter value close to that of the polymer, which is based on the rule of thumb of "like dissolves like." In spite of some restrictions on the solubility parameter theory, this approach is popularly used for a first approximation of the affinity between materials. Based on this theory, it can be said that methanol has the strongest interaction with water since methanol has a solubility parameter δ_t closer to water than to other alcohols. From Table I, the strong interaction or affinity between methanol and water could be found to be attributed to both strong polar and hydrogen bonding, which is a typical characteristic observed in polar/polar constituent mixtures. It was reported²⁻⁴ that the strong interaction between permeants in a polar/polar mixture causes the coupled transport of the permeant constituents in both sorption and diffusion steps during the permeation process.

Figure 2 exhibits the swelling ratios of the hydrophilic PVA membrane with an alcohol content in various alcohol/water mixtures. For a 1-butanol/water mixture, phase separation occurred below 85 wt % of the alcohol content, so the swelling measurement was made in the range of an alcohol content higher than 85 wt %. The swelling ratio could be represented as a measure of the gross interactions of membrane/water, membrane/alcohol, and water/alcohol. When the interaction of each pair is stronger, more liquid will be sorbed into the membrane by a good affinity of the permeant toward the membrane material or the coupling sorption of a permeant in the presence of the other permeants in the membrane, and, thereby, the resulting membrane is

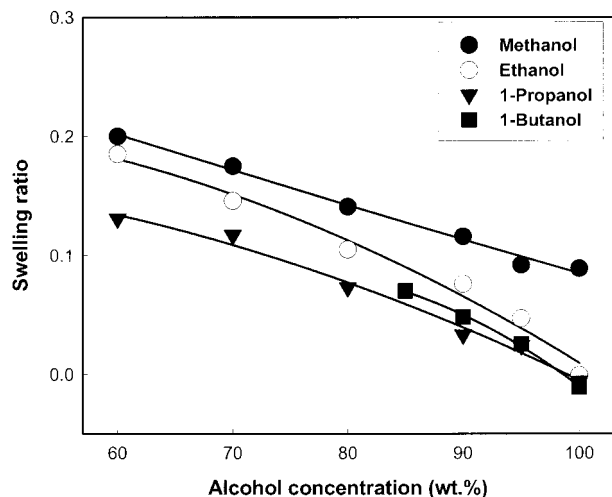


Figure 2 Swelling ratio of PVA membrane with alcohol content in alcohol/water mixtures at 30°C.

able to be more swollen. In the alcohol/water solutions, the magnitude of the swelling ratio of the PVA membrane was found to be in the order of the alcohol solubility parameter. However, with an alcohol content below 93 wt %, a 1-butanol/water solution shows some deviation: a higher swelling ratio than the 1-propanol/water solution, although the solubility parameter of 1-butanol is lower. The reason for that is not clear but it might be due to a complicated relationship of the swelling behavior with the interactions in the ternary system (water/alcohol/membrane).

Effect of Feed Composition on Permeation

Figures 3–5 present the permeation rates and separation factors of the water/alcohol mixtures with feed composition at different feed temperatures. For both the 1-propanol and 1-butanol aqueous mixtures, the alcohol contents in the permeate were too small to be detected by the GC used in this study, so that separation factors for the mixtures could not be presented here. For all the mixtures, the permeation rate increased and the separation factor decreased with increasing water content due to the increasing of the plasticization action of the water molecules.⁵ These observations are normal in the permeation of an aqueous solution through a hydrophilic membrane. The magnitude of separation factors were inversely proportional to the swelling ratio: methanol < ethanol < 1-propanol < 1-butanol.

In the region of high alcohol content above 92 wt %, the permeation rates of the mixtures were

in the order of the swelling ratio: methanol > ethanol > 1-propanol > 1-butanol. In this region of alcohol content, since the main component of the mixtures was alcohol, the permeation behavior could obviously be affected by the interaction between the alcohol and the membrane, that is, an affinity of alcohol toward the membrane. In other words, an alcohol having better affinity toward the membrane could be sorbed more into the membrane, increase the membrane mobility, and then permeate faster in the membrane.

However, when the alcohol content in the feed decreased below 90 wt %, surprisingly, the magnitude order of the permeation rate was the opposite: methanol < ethanol < 1-propanol < 1-butanol. It is very interesting to note that with increasing the solubility parameter of alcohol as going from the 1-butanol to the methanol mixture the permeation rate decreased although the solubility of alcohol in the membrane increased and its molecular weight decreased. Considering the

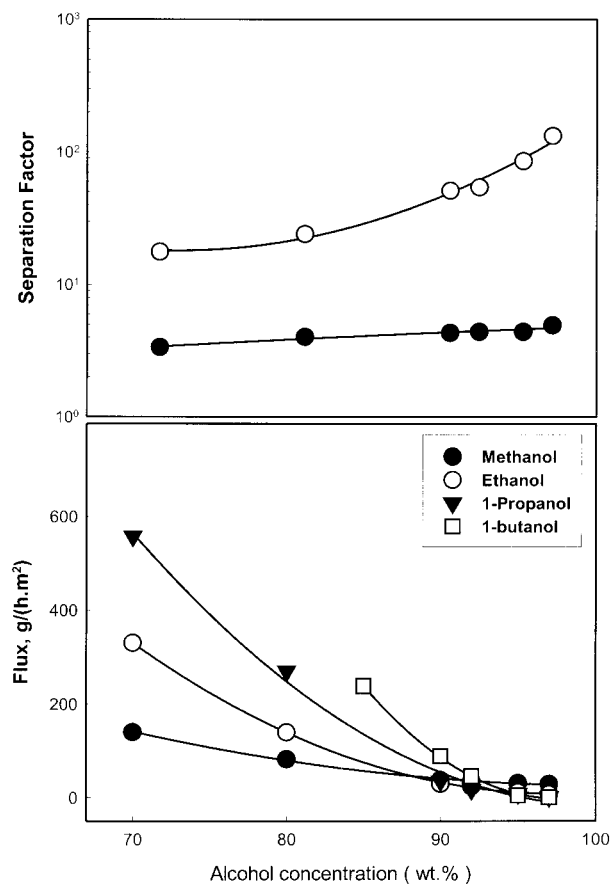


Figure 3 Plots of flux and separation factor with alcohol content in various alcohol/water mixtures at 30°C.

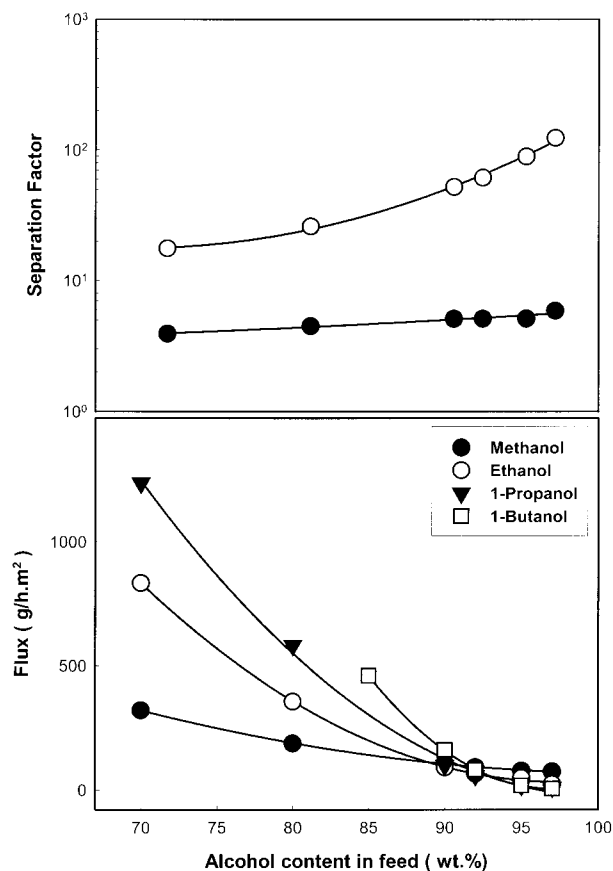


Figure 4 Plots of flux and separation factor with alcohol content in various alcohol/water mixtures at 40°C.

observation only from the solution-diffusion mechanism in which the permeation rate is expressed as the product of the diffusivity and the solubility of the permeant, it could be presumed that the decrease of the flux with increasing the solubility parameter of alcohol is assigned to a decrease in the diffusion coefficient of the alcohol aqueous solution in the given alcohol content. Then, a question arises: "What makes the diffusion coefficient of the solution decrease with increasing the solubility parameter of alcohol?" The question might be answered with respect to the mutual interaction between water and alcohol molecules in each feed solution. It can be postulated that as the water content in the feed increases from the concentrated state more alcohol molecules are coupled or associated with water molecules, so that both the number and size of the associated unit can be increased. The tendency of the association between water and alcohol molecules will be stronger through hydrogen bonding

and polar interaction as going from a 1-butanol to a methanol aqueous solution. As a result, the methanol/water mixture contains larger and more associated units than do other alcohol/water mixtures, and the associated units behave as a diffusing unit. Generally, a bigger diffusing unit has a smaller diffusion coefficient. Therefore, the larger and more diffusing unit created through a strong association between alcohol and water molecules could cause slower permeation. From this point of view, the interaction between permeant molecules can be characterized as a kinetic factor. The postulation made above will be rationalized through the analysis of permeation with the feed temperature in next section.

In summarizing the feed composition effect, the interaction between the alcohol and the membrane was important to determine the permeation in the concentrated region while both the plasticization action of water and the interaction between the water and alcohol constituents were

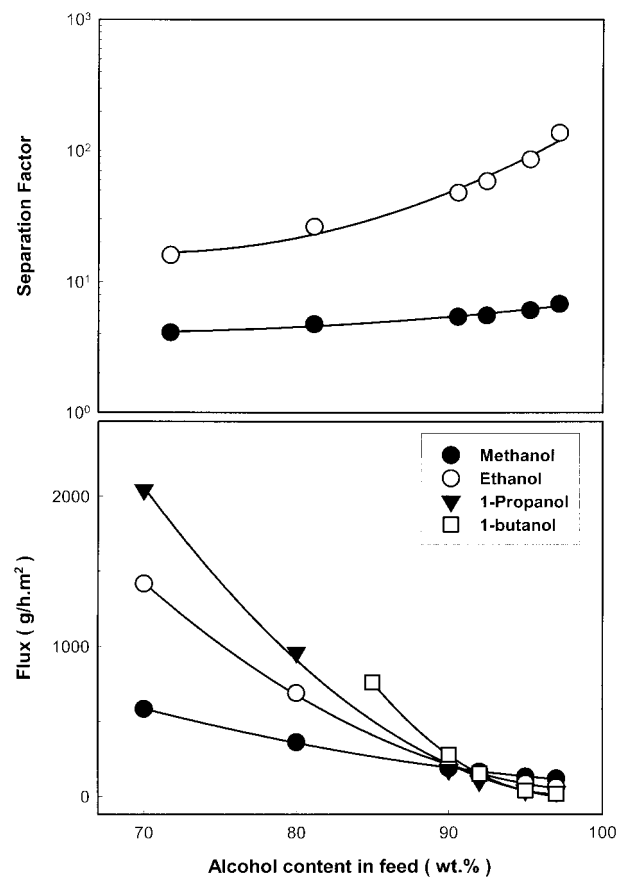


Figure 5 Plots of flux and separation factor with alcohol content in various alcohol/water mixtures at 50°C.

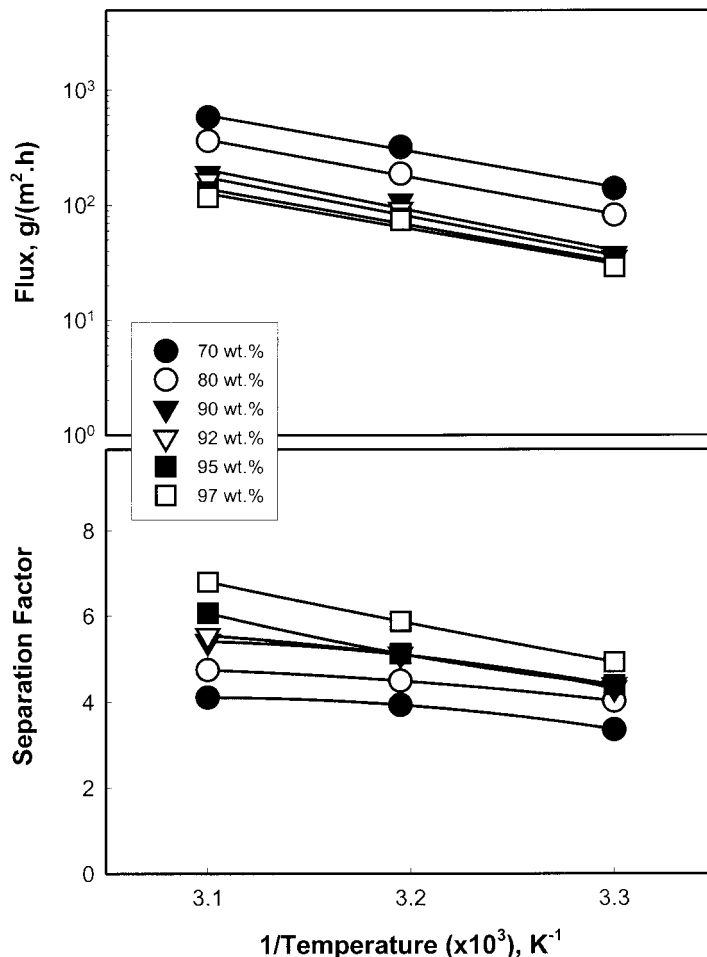


Figure 6 Plots of flux and separation factor with feed temperature in the permeation of methanol/water mixtures at different feed compositions.

significant to influence the permeation and separation of the mixture to a great extent in the region of low alcohol content. The plasticization action and the association of permeant molecules affect the permeation rate in an opposite way as mentioned above.

Effect of Feed Temperature on Permeation

Generally, the permeation at various feed temperatures is thought to be governed by the following three changes⁵:

- Change in the solubilities of the permeants
- Change in the free volume in the polymeric membrane created by the thermal motion of the polymer chains, that is, membrane mobility
- Change in the interaction between the permeants.

Figures 6–9 show plots of membrane performances with the feed temperature at different feed compositions. In the plots of flux, the permeation rates increased with the feed temperature due to the corresponding changes mentioned above: increasing the solubility, membrane mobility, and weakening the interaction which gives a smaller diffusing unit. The temperature dependence of the permeation rate J can be expressed by an Arrhenius-type relationship:

$$J = J_0 \exp(-E_p/RT) \quad (3)$$

where J_0 is the preexponential factor; E_p , the apparent activation energy of permeation; and T , the operating temperature. Their Arrhenius plots of flux present a good linearity in the given temperature range.

Looking at the plots of the separation factors, the separation factor for the methanol/water mix-

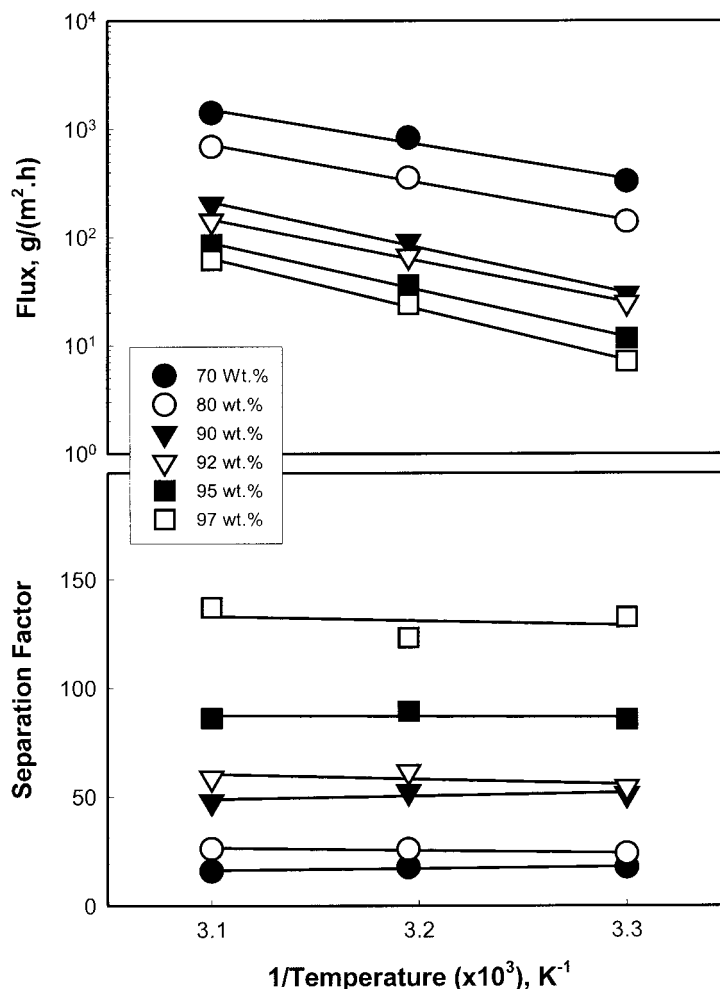


Figure 7 Plots of flux and separation factor with feed temperature in the permeation of ethanol/water mixtures at different feed compositions.

ture increased with increasing feed temperature while that for the ethanol/water mixture was not changed very much. In considering only coupling fluxes created by the membrane mobility and permeant solubility, the separation factor should be normally decreased, but the separation factor of the methanol/water mixture with the feed temperature showed the opposite tendency. This result also can be explained in terms of the interaction between the permeant constituents. In the methanol/water mixture, there are stronger interactions between methanol and water molecules than in the other alcohol/water mixtures as mentioned before. As the feed temperature increases, the interactions tend to weaken and there will be more possibility for reducing the associated unit size, resulting in forming more water molecules which are isolated or less associated with the alcohol molecules. So, water molecules having

better affinity toward the membrane will be permeating to greater extent than with methanol, increasing the separation factor. Now, it can be suggested that with increasing feed temperature the separation factor is increased by weakening the interactions between the permeant constituents (hereafter called the "interaction effect"), whereas it is decreased by the coupling fluxes (hereafter called the "coupling flux effect"). Therefore, these two effects influence the separation in the opposite way, so the separation factor increases or decreases with the feed temperature, depending on which effect is predominant. For a mixture having a strong interaction between the permeant constituents such as the methanol/water mixture, the interaction effect is predominant so that the separation factor can be increased with the feed temperature. In the case of the ethanol/water mixture which has less interaction

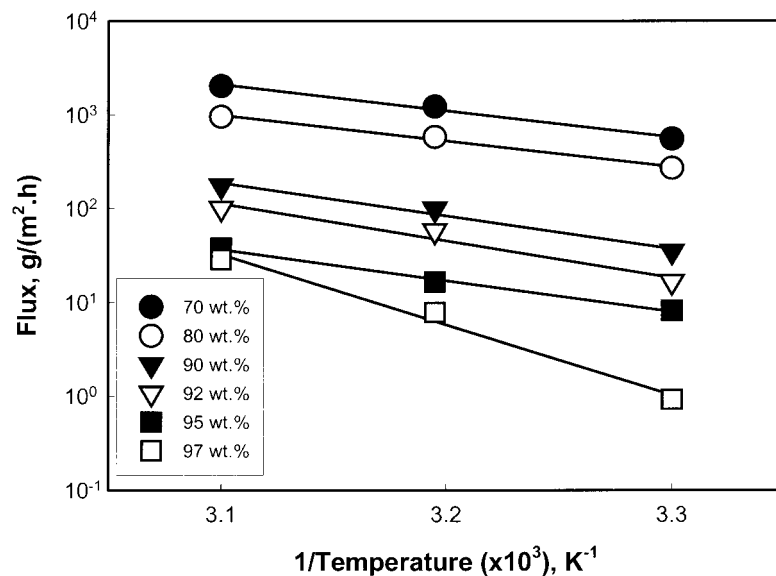


Figure 8 Plots of flux and separation factor with feed temperature in the permeation of 1-propanol/water mixture at different feed compositions.

between the permeants, these two effects are comparable. That is why the separation factor shows no specific tendency with the feed temperature. As a result, the separation data can support the fact that the interaction between permeants contributes to the permeation and separation of polar/polar mixtures.

More details on the interaction can be discussed through an analysis of the permeation ac-

tivation energy. Figure 10 shows the apparent activation energies with the feed composition in the permeation of each alcohol/water mixture. The permeation activation energies were determined from the slopes of the Arrhenius plots of flux shown in Figures 6–9. In this study, the permeation behavior of the binary mixture composed of polar–polar components through the PVA membrane at a given feed composition might

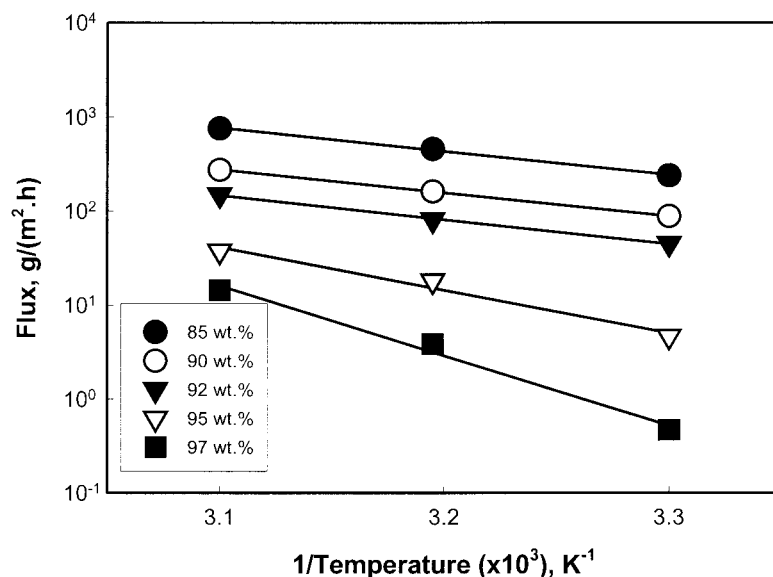


Figure 9 Plots of flux and separation factor with feed temperature in the permeation of 1-butanol/water mixture at different feed compositions.

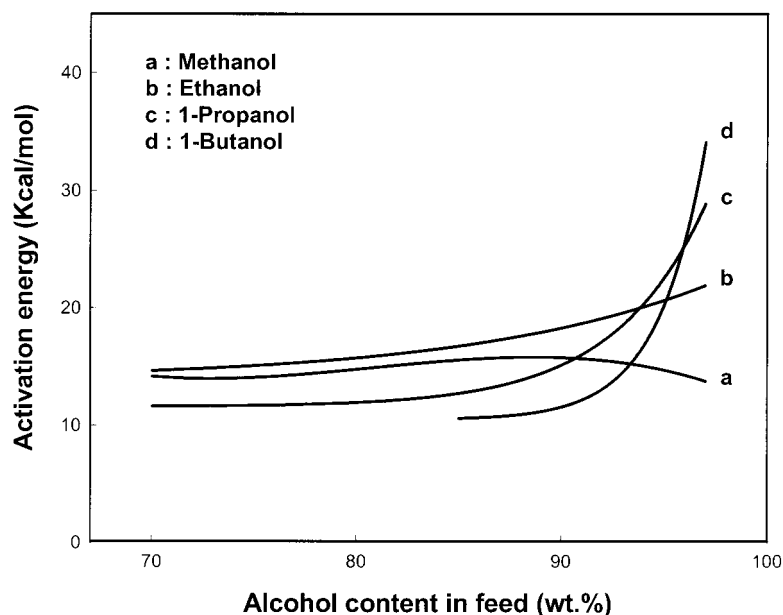


Figure 10 Apparent activation energy with alcohol content in various alcohol/water mixtures.

be affected mainly by both the interaction of the alcohol/water and the swelling ratio. In high alcohol contents above 92 wt %, in which alcohol is a major component, the magnitude order of the permeation activation energy of the solutions is observed to be consistent with the order of their swelling ratio. When interaction between an alcohol and a membrane is strong, the permeant molecules can be easily sorbed into the membrane and they make the membrane mobility increase by their plasticization action on the membrane, requiring less activation energy for permeation. However, as the water content in the feed is increased further, the permeation behavior could be affected by the following two changes:

- Increasing the water amount sorbed into the hydrophilic membrane, increasing the membrane mobility, and then decreasing the permeation activation energy
- Increasing the number of water molecules associated with the alcohol, increasing the permeating unit size, and then increasing the permeation activation energy.

Thus, the permeation can be contributed by these two combined effects which are opposite. With increasing water content, the permeation activation energy decreases by the change in the first term and, at the same time, it can decrease by the change

in the second. For a feed mixture having a stronger interaction between the permeant constituents, the contribution of the second one is more significant. Therefore, with increasing water content, the permeation activation energy decreased less when going from 1-butanol to the methanol mixture. As a result, in alcohol contents below 90 wt %, the magnitude order of the permeation activation energy was reversed. The result of the analysis of the permeation activation energy has a good agreement with the postulation made in the previous section.

CONCLUSIONS

In pervaporation of a homologous series of alcohol aqueous mixtures through hydrophilic poly(vinyl alcohol) (PVA), the sorptional and permeation behaviors of the feed mixtures through the hydrophilic membrane were discussed in terms of both the plasticizing effect and interaction effect of the permeant molecules in the membrane. With a high alcohol content above 92 wt %, the permeation rate was increased by the plasticizing effect in the order of the interaction strength between the alcohol and water in the feed. However, for a low alcohol content below 90 wt %, the tendency of the permeation rate was found to be opposite by the interaction effect, indicating that the interactions between the permeant and the permeant constituents play an im-

portant role in determining the permeation and separation of the mixtures. Especially, for the methanol/water mixtures having the strongest interaction between the permeant constituents, the separation factor increased with increasing feed temperature, which is a result of the weakening the interactions between methanol and the water molecules. This study also suggested that as the interaction between permeant constituents in a mixture is stronger the interaction effect is more significant in determining the permeation and separation characteristics.

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