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Abstract: The characteristics of permeation and separation of acetic acid-water mixtures through 85/15 (v/v) poly(vinyl alcohol)/malic acid (PVA/MA) membranes were investigated by evapomeation (EV) and temperature difference controlled evapomeation (TDEV) methods. The effects of permeation temperature, membrane surrounding temperature, and feed composition on the permeation rate and the separation factor were studied. The permeation rates increased but separation factors decreased with an increase in permeation temperature in EV method. Permeation activation energy of acetic acid and water in the evapomeation were calculated as 107.4 kJ/mol and 36.5 kJ/mol, respectively, using an Arrhenius type relationship. When the temperature of feed solution was kept constant and the temperature in the membrane surrounding was dropped, it was observed that the permeation rate and separation factor were significantly influenced by the temperature of membrane surroundings. The increase in the acetic acid concentration in the feed vapor mixture decreased the permeation rate and increased the separation factor except 40 wt.%

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acetic acid content. The best separation factor was found at a composition of 90 wt.% acetic acid as 800 in the EV and 860 in the TDEV. Separation index in both methods were also calculated, the separation index of TDEV method was found to be higher than that of EV method for azeotropic composition of acetic acid-water. TDEV method for separation of acetic acid-water mixtures through the PVA/MA membranes was found to be more effective than evapomeation method.

Keywords: Evapomeation, Temperature difference controlled evapomeation, Acetic acid-water mixtures, Poly(vinyl alcohol) membranes, Separation

INTRODUCTION

Pervaporation has been recognized as a promising separation process because of its effective and economical separation of liquid mixtures, especially, water-organic mixtures with an azeotrop and/or small differences in boiling characteristics (1–3). In many industrial processes, acetic acid is an important chemical intermediate; in the synthesis of vinyl acetate, terephthalic acid, cellulose esters, and esters. However, an account of the small differences in the volatility of water and acetic acid in aqueous solutions shows the separation of acetic acid from water is an energy-expensive process, from an energy-saving standpoint. For this recently, attention has been focused on the dehydration of acetic acid by pervaporation (4–12). In the pervaporation of acetic acid mixtures several membranes were employed, such as silicalite (6), charged Nafion (8), silicalite-filled polydimethylsiloxane (9), asymmetric polycarbonate (12), and poly(4-vinyl pyridine-co-acrylonitrile) (13), with low permeation rates and separation factors compared to the membrane employed for the separation of ethanol/water mixtures. When these membranes were used in pervaporation, their chemical and physical properties are often deteriorated by swelling or shrinking of the membrane, caused by the direct contact with the feed mixtures.

Uragami et al. (14–18) proposed an evapomeation method (Fig. 1a) as a new membrane separation technique that has the advantages of pervaporation (PV) but not its disadvantages. In evapomeation, the membranes are not in direct contact with the feed mixtures, only vapors are supplied to the membranes. Therefore, swelling or shrinking of the membranes due to the feed mixtures can be largely prevented and consequently an improvement of membrane performance may be expected. They have discussed the characteristics of permeation and separation of aqueous alcohol solutions through polystyrene and poly(vinyl chloride) (14), alginic acid (15), chitosan derivatives (16), modified silicone rubber (17), polyvinyl alcohol γ-ray grafted Nylon 4 (18) membranes by EV and compared with those by PV. They have also proposed the TDEV method that can establish a temperature difference between the feed solution and the membrane surroundings (19). For aqueous alcoholic solutions

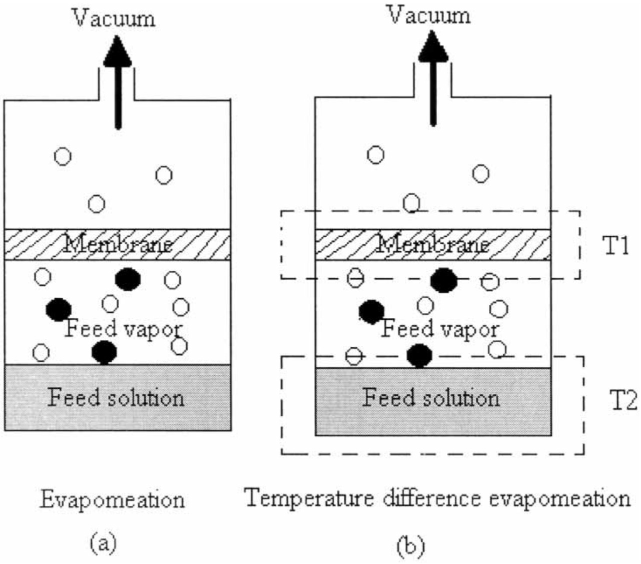

Figure 1. Principal scheme of the evapomeation (a) and temperature difference controlled evapomeation (b) methods.

modified silicone rubber (17) and polydimethylsiloxane (19) membranes showed a very high permselectivity for alcohol in the TDEV method.

Poly(vinyl alcohol) has been studied intensively as a membrane material because of its good chemical-resistant properties. Membrane selectivity can generally be increased through the modification of the chemical structure of polymers by crosslinking, grafting, etc. Rhim et al. (20) modified the poly(vinyl alcohol) using sulfur succinic acid. Lee et al. (21) studied pervaporation separation of ethanol-water mixtures using PVA membrane crosslinked with low molecular weight of poly(acrylic acid).

In our previous study (22), we have used PVA membranes modified with malic acid (hydroxy succinic acid), and optimum PVA/MA ratio, membrane thickness, and operating temperature were determined for pervaporation of acetic acid-water mixtures. In this paper, we have aimed to investigate separation and permeation characteristics of acetic acid-water mixtures through 85/15 PVN/MA membranes by EV and TDEV methods.

EXPERIMENTAL

Materials

PVA was purchased from Merck (Darmstadt, Germany). The molecular weight and the degree of saponification were 72,000 and >% 98, respectively.

MA (98 wt.%) was Sigma Chemical Co. product. Acetic acid (extrapure grade) was supplied by Merck.

Membrane Preparation

Aqueous 5 wt.% PVA solutions were prepared by dissolving preweighed quantities of dry PVA in water and heated at 90°C at least 6 h. Then the PVA solution was mixed with 5 wt.% MA solutions at 85/15 PVN/MA composition and stirred for at least 1 day at room temperature to form homogeneous solution. Membranes were cast onto petri dishes and the solvent was evaporated at 30°C to form the membrane. The dried membranes were heated in a termosetted oven for 1 h at 150°C. The thickness of the resulting membranes showed 80 μm. The prepared membranes were then stored in distilled water for further use.

Infrared Analysis

Infrared spectroscopy (IR) spectra of PVA and 85/15 PVA/MA membranes were taken with Mattson 1000 Fourier transform infrared spectrometer.

Differential Scanning Calorimetry (DSC)

The thermal analysis was performed with General V4.1C Dupont 2000 differential scanning calorimeter. Sample weights ranged from 5 to 8 mg. The samples were heated from 50 to 250°C at a heating rate of 10°C/min. The intercept point of slopes was taken as the glass transition temperature (T_g).

Swelling Measurement

The dried membranes were exposed to the vapor of acetic acid solutions at 25°C for at least 48 h. The membranes were weighed as quickly as possible, after being wiped with cleansing tissue. Then the membranes were dried in a vacuum oven at room temperature until constant weight. The swelling degrees, (SD), of membranes were determined as follows:

$$\mathrm{SD} = \frac{(\mathrm{Ws} - \mathrm{Wd})}{\mathrm{Wd}} \times 100 \tag{1}$$

where Ws is the weight of the membrane swollen in the feed vapor, and Wd the weight of the dry membrane.

Evapomeation and Temperature Difference Controlled Evapomeation

Evapomeation and temperature difference controlled evapomeation were carried out using the apparatus shown in Fig. 2. The permeation cell with jacked was assembled from two half cells made of glass, fastened together by joints. The capacity of each cell was about 150 mL. Membranes were placed on to the porous glass support in the cell. The effective membrane area was 12.5 cm^2. The reduced pressure was kept at the 0.7 mbar with a vacuum pump (Edwards, U.K.). The mixture of acetic acid and water was used as a feed solution. EV experiments were conducted at constant temperatures ranging 30–50°C using 20 wt.% acetic acid composition. The feed mixture was circulated to prevent concentration polarization with peristaltic pump (Unitest, Turkey) through the cell from the feed tank, which was kept in a constant temperature water bath. In TDEV method the temperature of the feed solution was kept constant at 40°C and the temperature of membrane surroundings was changed in the range of 0–40°C. Upon reaching steady-state flow conditions the permeate vapor was collected in liquid nitrogen traps and weighed. The composition of permeates was deducted by measuring the refractive indicates with Atago DD-5 type digital differential refractometer (Atago Co., Ltd., Japan). Performance of evapomeation and temperature difference controlled evapomeation was expressed by separation factor (selectivity), permeation rate (flux), and separation index (SI).

The separation factor was defined as follows:

$$\alpha = \frac{(\mathrm{P}_{\text{water}}/\mathrm{P}_{\text{acetic acid}})}{(\mathrm{V}_{\text{water}}/\mathrm{V}_{\text{acetic acid}})} \tag{2}$$

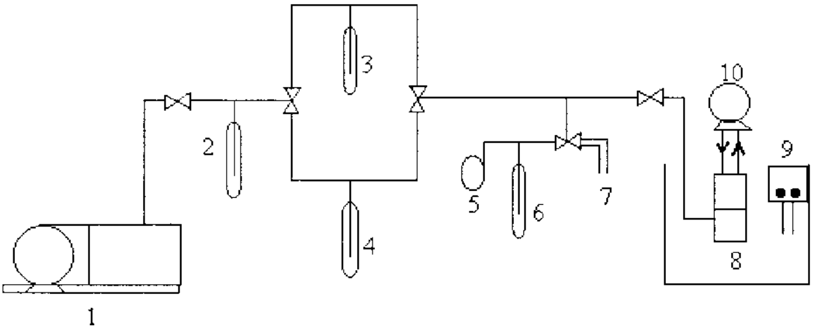

Figure 2. Schematic diagram of evapomeation and temperature difference controlled evapomeation apparatus used in this study. 1. Vacuum pump 2,3. Trap 4,6. Cold traps for collecting samples 5. Vacuum monometer 7. Vent to atmosphere 8. Permeation cell 9. Water bath with temperature indicator 10. Peristaltic pump.

where P_{water}, $P_{acetic\ acid}$, and V_{water}, $V_{acetic\ acid}$ are the weight fractions of water and acetic acid in the permeate and feed vapor, respectively.

The permeation rate (J) was determined by using the following equation:

$$J = \frac{Q}{A.t} \tag{3}$$

where Q, A, and t represent the weight of the permeate (kg), effective membrane area (m^2), and operation time (h), respectively.

The evapomeation and temperature difference controlled evapomeation separation index are calculated by using the following equation:

$$SI = J.\alpha \tag{4}$$

where J and α are the total permeation rate and separation factor, respectively.

RESULTS AND DISCUSSION

IR Spectra Analysis and DSC Results

IR spectra of PVA and 85/15 PVA/MA membranes were shown in Fig. 3. As it is seen from the Fig. 3 the absorptions at 1725 cm^{-1} are typical to the ester (-CO-O-) band (4) and the peak intensity of this carbonyl band increased with the MA content. The 1182 cm^{-1} peak arose from the C-O stretch mode in ester group and 918 cm^{-1} was the O-H out of plane motion of the carboxylic group in MA. While the C-O stretch mode increased, the peak intensity of O-H out of plane motion decreased due to the reaction. It is clear that the spectral changes are evidences of crosslinking reaction between the hydroxyl group of PVA and the carboxylic group of MA (Fig. 4).

T_g plays an important role in determining the membrane performance since high or low T_g makes a polymer tough and rubbery, which affects the permeability of membrane. The PVA polymer used in this study showed a T_g of 92°C, however, this value for 85/15 PVA/MA has been found to be 95°C. The increase in T_g could also be the evidence of the crosslinking reaction between MA and PVA in the membrane.

Effect of Feed Composition in Evapomeation

Figure 5 shows the effect of the acetic acid concentration (20–90 wt.% acetic acid) on the permeation rate and separation factor for the 85/15 PVA/MA and PVA membranes at a feed solution temperature of 40°C in EV (22). In this range of feed composition the permeation rate decreased continuously whereas separation factor decreased up to 40 wt.% acetic acid content in

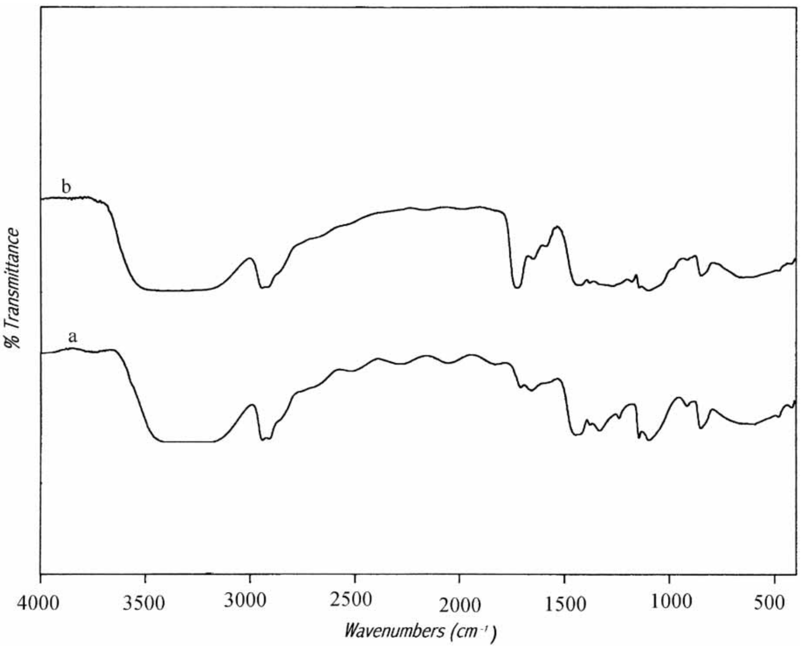

Figure 3. IR spectra of PVA (a) and 85/15 PVA/MA (b) membranes.

feed solution then increased sharply as the acetic acid concentration in the feed vapor increased. Also as can be seen from the figure, separation factors of PVA/MA membrane were better than that of PVA membrane whereas permeation rates of PVA membrane were higher than PVA/MA membrane due to crosslinking reaction depicted in Figs. 3 and 4 and the DSC results. When the malic acid was added, carboxyl groups of acid react with the hydroxyl groups of the PVA resulting crosslinking in the membrane. Thus membrane has less solubility of a liquid, therefore both solubility and

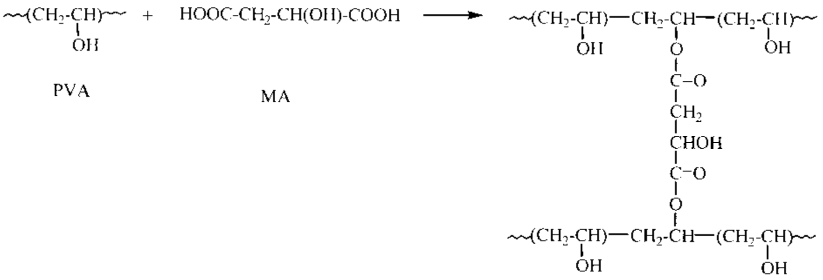

Figure 4. Postulated reaction mechanism of PVA with MA.

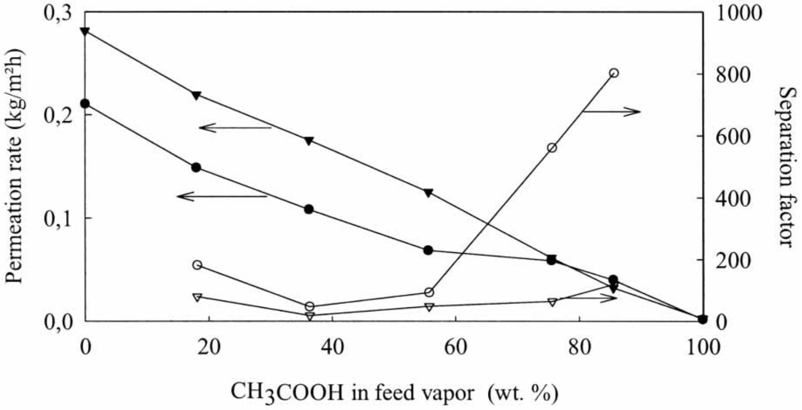

Figure 5. Effect of acetic acid composition in feed vapor on permeation rate and separation factor through PVA/MA (●, ○) and PVA (▲, △) membranes by EV at 40°C. Permeation conditions: membrane thickness: 80 μm, pressure: 0.7 mbar.

diffusivity of permeating liquid through the membrane decline, which depresses the permeation rate and increases the separation factor.

The transport mechanism on evapomeation through polymeric membranes can be described by solution-diffusion model. The membrane performance depends upon sorption of permeants in feed vapor and their diffusion through the membrane (15). In evapomeation system, when the permeating side is vacuumed, the feed solution is vaporized. The vaporized molecules contact with the membrane, dissolve in, then diffuse through and evaporate from the membrane (15) named as solution diffusion mechanism. When the transport of species through the membrane is due to this mechanism, the size of the permeating species is very important in the solution or diffusion processes (14). The molecular size of water (0.28 nm) is smaller than acetic acid (0.40 nm) (6). In addition, water has much more hydrophilic character than acetic acid. Therefore water molecules in evapomeation can be selectively incorporated into the hydrophilic membrane and predominantly diffused. Consequently permeation rate decreases with the decrease in the water vapor content of the feed. As can be seen from Fig. 5, separation factor first decreased then increased with the acetic acid concentration in the feed vapor. Decrease of separation factor up to 40 wt.% acetic acid content can be attributed to the swelling action of water vapor on the membrane. Figure 6 shows the change of the swelling degree with the acetic acid content in the feed vapor. As it is seen from the figure swelling of PVA/MA, membrane increases up to 40 wt.% acetic acid content due to plastizating action of water vapor on the membrane, then decreases. Increase in the swelling of the membrane up to 40 wt.% acetic acid content

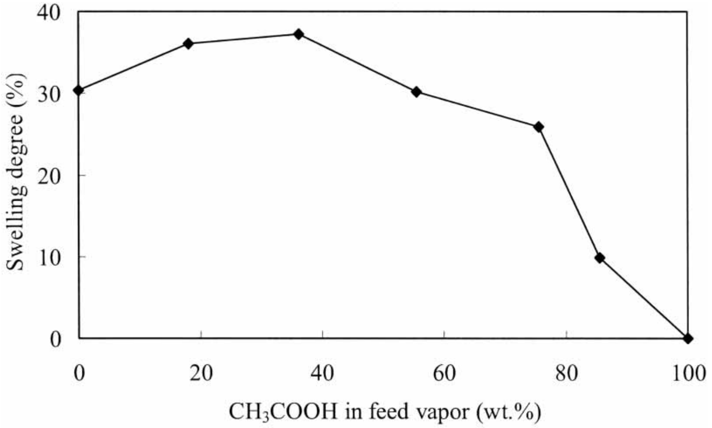

Figure 6. Change of swelling degree (%) with feed vapor composition.

causes an increase in the acetic acid permeation. Hence separation factor decreases up to this composition. Increase in the separation factor after that concentration can be attributed to the association of acetic acid molecules and the difficulty in the permeation of associated molecules through the membrane. Similar results were observed in the literature in pervaporation (23).

Looking at the permeation rate of each individual component in Fig. 7, water permeation rate is too large compared with that of acetic acid, so the shape of the water permeation rate curve is almost similar to that of total permeation rate. Water permeation rate decreased with acetic acid vapor content as total

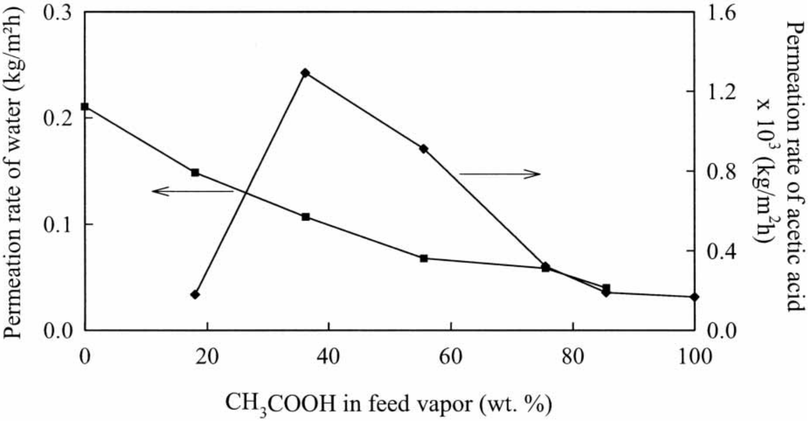

Figure 7. Variation of permeation rate of water (■) and permeation rate of acetic acid (◆) with feed vapor composition.

permeation rate did, while acetic acid permeation rate has a maximum value at around 40 wt.%, that is, permeation enhancement of acetic acid was found.

Only one study was found concerning the effect of the feed (acetic acid) composition on evapomeation in the literature. Uragami (24) studied separation of aqueous acetic acid solutions through hydrophobic poly(vinyl chloride) membranes. He observed the same trend that permeation rate decreases with acetic acid concentration in the range of 0–100 wt.% acetic acid in the feed at 40°C. However permeation rates founded in our study using hydrophilic PVA/MA membrane (0.002–0.211 kg/m^2h) were higher than that study (~0.003–0.007 kg/m^2h) at 40°C.

Effect of Permeation Temperature In Evapomeation

The effect of permeation temperature on the total permeation rate and separation factor for aqueous solution of 20 wt.% acetic acid in evapomeation is shown in Fig. 8 in which the temperature of both the feed solution and membrane surroundings were equal. As can be seen from the figure, permeation rates increased, but separation factors decreased with increasing permeation temperature. As temperature increases, the frequency and amplitude of PVA/MA chain jumping increase and the resulting free volume becomes larger. In evapomeation, permeating molecules can diffuse through these free volumes. Thus the diffusion rates of both isolated and associated permeating molecules increase with the temperature so that permeation rate could be higher and separation factor lower. Similar results were found in literature (14, 17, 25).

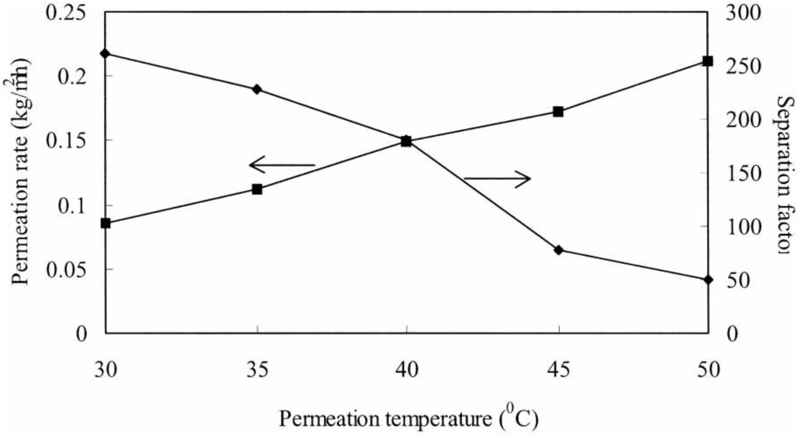

Figure 8. Effect of permeation temperature on the total permeation rate (■) and separation factor (◆) in EV. Permeation conditions: 20 wt.% CH_3COOH, membrane thickness: 80 μm, pressure: 0.7 mbar.

Arrhenius Plot of Permeation Rate

The temperature dependence of permeation rate can be expressed by an Arrhenius type relationship (23).

$$Jp = Ap.\exp(-Ep/RT) \tag{5}$$

where Ap and Ep are the pre-exponential factor and the apparent activation energy of permeation, respectively. Figure 9 shows Arrhenius plots of individual permeation rates which are used to calculate the permeation activation energies. The permeation activation energy of water and acetic acid are calculated to be 36.5 kJ/mol and 107.4 kJ/mol, respectively. The solubility of acetic acid vapor in the membrane was smaller than water, leading to larger heat of solution (ΔH), and acetic acid having larger permeating molecule size can have higher diffusion activation energy (Ed) than the case of water. Thus Ep of acetic acid is calculated to be larger than that of water for 20 wt.% acetic acid (Eq. 6).

$$Ep = \Delta H + Ed \tag{6}$$

Membrane Performance in Temperature Difference Controlled Evapomeation Method

The permeation and separation characteristics for an aqueous solution of 20 wt.% acetic acid through the 85/15 PVA/MA membrane in TDEV, in

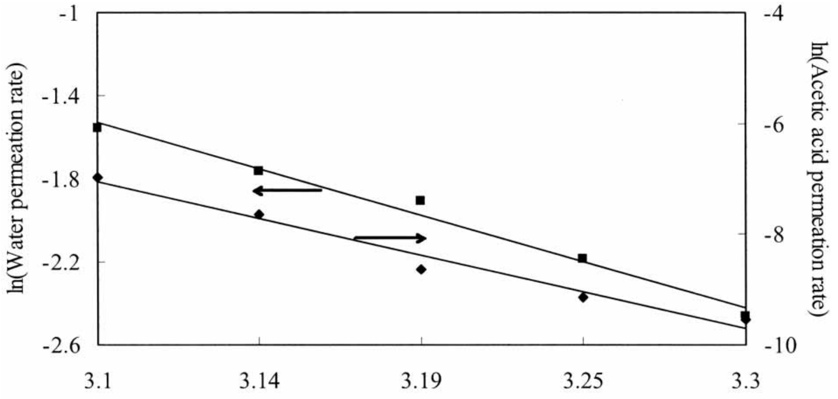

Figure 9. Arrhenius plot of ln(water permeation rate) (■) and ln(acetic acid permeation rate) (◆) with 1/Temperature for PVA/MA membrane.

which the temperature of the feed solution was kept constant at 40°C and the temperature of the membrane surrounding was changed in the range of 0–30°C, are shown in Fig. 10. The permeation rate increased continuously but the separation factor toward water decreased with the membrane surrounding temperature. When the acetic acid and water molecules are vaporized, these vaporized molecules come close to the membrane surroundings kept at a lower temperature, the acetic acid molecules are liable to be aggregated more than the water molecules [because the freezing point of acetic acid (16.7°C) is higher than that of water (0°C)]. It is very difficult for these aggregated acetic acid molecules to be incorporated into the PVA/MA membrane and be diffused through the PVA/MA membrane. This aggregation of acetic acid is responsible for the increase of separation factor toward water through the PVA/MA membrane. Similar results were found in literature (17, 24–26).

Uragami et al. (17) studied permeation and separation characteristics for aqueous alcoholic solutions through a modified silicone rubber membrane containing poly(propylene glycol) by both pervaporation and evapomeation. They observed that when the temperature of the membrane surroundings was kept constant and the temperature of aqueous ethanol solution was varied, or vice versa, the permeation rate and the permselectivity for ethanol are significantly influenced by the temperature in each permeation condition. When the temperature of feed solution was kept constant at 40 or 70°C and that of the membrane surrounding was varied (−30–0°C), they observed that the permeation rate for 10 wt.% ethanol solution decreased due to the lowering of both the motions of polymer chains constituting the membrane and the activity of permeants.

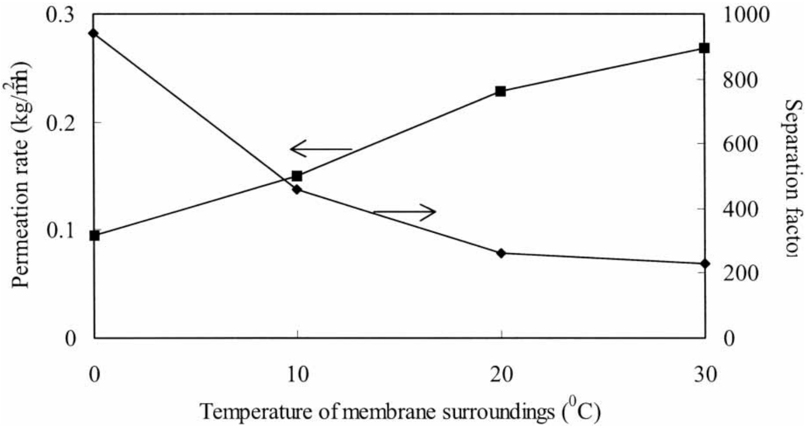

Figure 10. Effect of membrane surroundings temperature on the permeation rate (■) and separation factor (◆). Permeation conditions: 20 wt.% CH_3COOH, membrane thickness: 80 μm, temperature of feed solution: 40°C, pressure: 0.7 mbar.

Uragami et al. (26) also investigated permeation and separation characteristics for aqueous alcoholic solutions using a poly(dimethylsiloxane) membrane by pervaporation and evapomeation in their other work. They found that the permeation rate decreased, but the permselectivity for ethanol increased remarkably with dropping temperature in the membrane surroundings. When the temperature of feed solution was kept constant at 40°C and the temperature in the membrane surroundings was changed between the −30 and 0°C, the permeation rate decreased and separation factor remarkably increased with lowering of the temperature in the membrane surroundings as in our results.

Comparison of the Effect of the Feed Vapor Composition in EV and TDEV

The effect of acetic acid concentration on permeation rate and separation factor by EV and TDEV was shown in Fig. 11. The feed solution temperature was kept at 40°C in both EV and TDEV while membrane surrounding temperature was kept at 20°C in TDEV. It is reflected from the figures that both the permeation rates and separation factors in TDEV were higher than in EV due to the temperature difference between the feed mixture and the membrane surroundings. The best separation factor found at 90 wt.% acetic acid was 860 with the permeation rate of 0.045 kg/m^{2}h in TDEV method. The permeation rates with the TDEV method were higher than those of EV. When the membrane surrounding temperature dropped, the permeation rate increased due to occurange of temperature driving force. Freezing point of

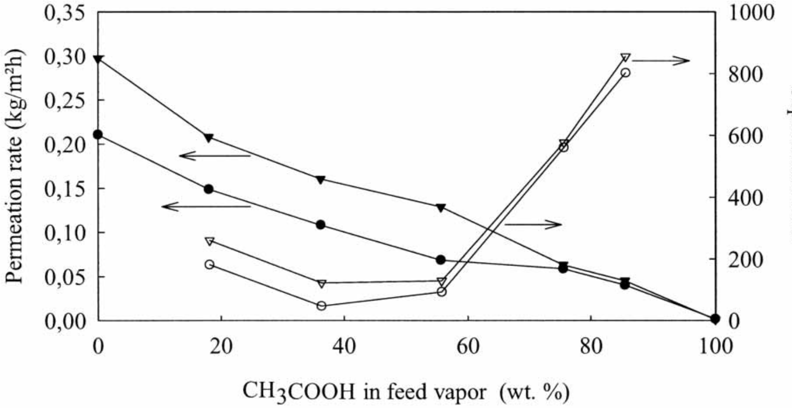

Figure 11. Comparison of permeation rate and separation factor of acetic acid-water solution through the PVA/MA membrane by evapomeation (●, ○) and temperature difference controlled evapomeation (▲, △).

acetic acid molecules is 16.7°C while that of water is 0°C. When the acetic acid and water molecules which had vaporized from the feed temperature come close to membrane surrounding, the acetic acid vapor aggregates much easier than the water vapor and tends to liquefy as the temperature of the membrane surroundings decreased to 20°C. This aggregation of acetic acid molecules is responsible for increase of separation factor for water through PVA/MA membrane in TDEV method.

Results of the studies reported in the literature on the separation of acetic acid-water mixtures were listed in Table 1 for comparison purposes. As can be seen from the table, malic acid crosslinked membranes have reasonable permeation rates and high separation factors compared to the other carboxylic acids or aldehydes crosslinked membranes. Furthermore the best separation factors were obtained in TDEV method.

The comparison of EV and TDEV methods bases on separation index were shown in Fig. 12. Separation indexes of TDEV method are much higher than that of EV method especially at low acetic acid concentrations. As a result, both methods are feasible in the separation of acetic acid water mixtures but the TDEV method is more effective than EV method with 85/15 PVA/MA membranes.

Separation of Acetic Acid-Water Azeotropic Mixture

Evapomeation and temperature-controlled evapomeation methods were applied to separate acetic acid water azeotropic mixtures (3 wt.% acetic acid with a boiling point of 76.6°C (28)). Table 2 shows the permeation and separation characteristics of azeotropic mixtures through the PVA/MA membrane. The feed temperature was set as 40°C for PV, EV, and TDEV and the temperature of the membrane surroundings was 20°C in TDEV. The permeation rates followed the order of PV $>$ TDEV $>$ EV, whereas the separation factors were in order of TDEV $>$ EV $>$ PV. Also SI of TDEV method for azeotropic composition was found to be higher than EV and PV methods.

Water predominantly permeated through the PVA/MA membrane in each method because of the hydrophilicity and smaller molecular size. As it is seen the permeation rates in PV were higher than that in EV. These results might be due to the fact that the membrane was in direct contact with the feed solution in PV and get more swollen. Thus, the diffusivity of the permeating species will be higher in PV than the other methods. Hence, the separation factors with PVA/MA membrane in PV will be lower than EV and TDEV. Table 2 also compares the three methods with respect to the SI value. The highest SI was obtained with TDEV at azeotropic composition. Hence it could be concluded that TDEV was better for separating aqueous acetic acid solutions than PV and EV with 85/15 PVA/MA membranes as far as separation factors were considered.

Table 1. Comparison of the performance of the membranes based on PVA crosslinked with different carboxylic acids or aldehydes for separation of acetic acid-water mixtures

Polymer	Nature of the membrane preparation method	Feed composition (%) (w/w)	Temperature (°C)	Permeation rate (J) (kg/m^2h)	Separation factor (α)	Separation method	Reference
PVA	Crosslinking with amic acid	10–90	30–75	0.08–2.28	13–42	PV	27
PVA	Crosslinking with maleic acid	10–90	25	∼0.40–2.00	∼5.0–7.8	PV	4
PVA	Crosslinking with glutaraldehyde formaldehyde	10–90 10–90	30 30	∼0.0001–0.0003 ∼0.0001–0.0004	∼4.0–9.0 ∼1.0–5.5	PV	11
PVA	Crosslinking with malic acid	20–90	40	0.05–0.29	120–670	PV	22
PVA	Crosslinking with malic acid	20–90	40	0.04–0.15	180–800	EV	This study
PVA	Crosslinking with malic acid	20–90	40 20*	0.05–0.21	260–860	TDEV	This study

*Membrane surrounding temperature.

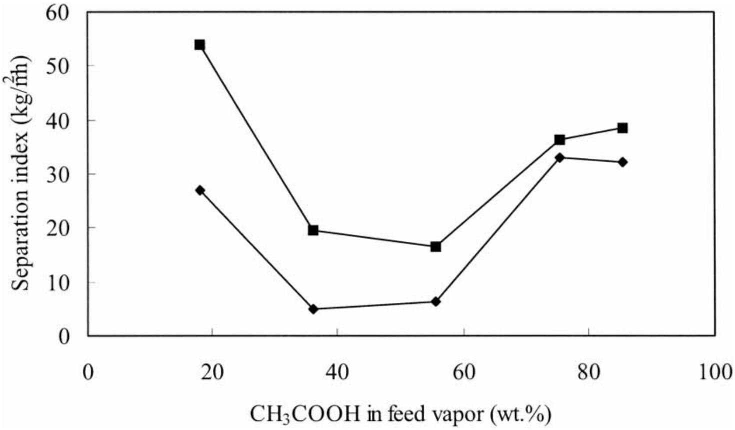

Figure 12. Change of separation index with feed vapor composition in EV (■) and TDEV (◆) method.

CONCLUSIONS

Separation of acetic acid water mixtures using PVA membranes crosslinked with MA (85/15 PVA/MA) has been studied using EV in which membranes are not in direct contact with the feed mixture, and TDEV in which a temperature difference between the feed solution and the membrane solution establishes. The effects of feed composition, permeation temperature, and membrane surrounding temperature on the permeation rate and separation factor were investigated. The evapomeation separation of acetic acid-water mixtures have been carried out in the range of 20–90 wt.% acetic acid contents in feed at 40°C. The membrane yielded good separation performance; permeation rates of 0.040–0.149 kg/m^{2}h and separation factors of 180–800 in EV method. In TDEV method permeation rates of 0.045–0.208 kg/m^{2}h and separation factors of 260–860 were

Table 2. Permeation and separation characteristics of acetic acid-water azeotropic mixture through PVA/MA membrane

Method	Permeation rate (kg/m^{2}h)	Separation factor	Separation index (kg/m^{2}h)	Reference
PV	0.33	23	7.6	22
EV	0.17	37	6.3	This study
TDEV	0.22	52	11.4	This study

obtained. Compared with PV(22), EV and TDEV processes have significantly high separation factors, however, permeation rates were low.

The permeation rate of PVA/MA membrane increased but separation factor decreased with the increase of the permeation temperature in evapomeation. The permeation rates in the permeation temperature range of 30–50°C are found to follow the Arrhenius law. The permeation activation energy for acetic acid (107.4 kJ/mol) was found to be much higher than that of water (36.5 kJ/mol).

When the temperature of feed solution was kept constant at 40°C and temperature of membrane surroundings was set lower than the temperature of feed solution, the separation factor for water in aqueous acetic acid solution through the PVA/MA membrane was significantly improved.

Also permeation and separation characteristics of azeotropic composition of acetic acid-water mixture through PVA/MA membrane were investigated; permeation rate of 0.171 kg/m^{2}h, 0.215 kg/m^{2}h, and separation factor of 37, 52 were found in EV and TDEV, respectively.

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