Permeation and Separation Characteristics of Acetic Acid/Water Mixtures through Poly(vinyl alcohol-*g*-itaconic acid) Membranes by Pervaporation, Evapomeation, and Temperature-Difference Evapomeation

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ABSTRACT: In this study, itaconic acid (IA) was grafted onto poly(vinyl alcohol) (PVA) with cerium(IV) ammonium nitrate as an initiator at 45°C. The grafted PVA was characterized with Fourier transform infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, and differential scanning calorimetry. IA-grafted PVA membranes were prepared with a casting method, and the permeation and separation characteristics of acetic acid/water mixtures were investigated with pervaporation (PV), evapomeation (EV) and temperature-difference evapomeation (TDEV) methods. The effects of the feed composition, operating temperature, and temperature of the membrane surroundings on the permeation rate and separation factor for the acetic acid/water mixtures were studied. The permeation rates in EV were lower than those in PV, whereas the separation factors were higher. With the TDEV method, the permeation rates decreased and the separation factors increased as the temperature of the membrane surroundings decreased. The prepared membranes were also tested in PV, EV, and TDEV to separate the various compositions of the acetic acid/water mixtures (20–90 wt % acetic acid) at 40°C. The highest separation factor, 686, was obtained in TDEV with a 90 wt % acetic acid concentration in the feed. The activation energies of permeation in PV and EV were calculated to be 8.5 and 10.2 kcal/mol, respectively, for a 20 wt % acetic acid solution. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2322–2333, 2004

Key words: graft copolymers; membranes; separation techniques

INTRODUCTION

The recently developed pervaporation (PV) process is a quite attractive separation process[1–5] that has the advantages of simplicity, low cost, an acceptable permeation rate (flux), and a high separation factor (selectivity), which make it a promising separation process for the separation and dehydration of azeotropic, close-boiling, and aqueous organic mixtures. However, with the PV method, polymer membranes are swollen or shrunk because the feed solutions are directly in contact with the polymer membrane, and so the original functionalities of the polymer membranes, designed chemically and physically, are sometimes impaired by the swelling or shrinking of the membranes.[6,7] Therefore, Uragami and coworkers[7,8] proposed an evapomeation (EV) method as a new membrane separation technique having the advantages of PV but not its disadvantages.

Permeation and separation characteristics for aqueous alcohol solutions by EV have been investigated with various polymer membranes derived from polystyrene, poly(dimethylsiloxane), modified silicon rubber, alginic acid, and chitosan.[6–10] These membranes with the EV method predominantly permeate water from aqueous alcohol solutions and show high separation factors. Moreover, with a certain EV method, a temperature difference between the feed solution and the membrane surroundings can be established. This method is called temperature-difference evapomeation (TDEV), and the permeation and separation characteristics of poly(dimethylsiloxane) membranes for aqueous alcohol solutions with the TDEV method have been reported.[7]

Although many articles have focused on the separation of aqueous alcohol systems,[11–18] the separation of other mixtures has received relatively little attention. Acetic acid is a very important organic intermediate used, for example, in the synthesis of vinyl acetate, terephthalic acid, cellulose esters, and esters in the chemical industry.[19–22] Because of the small differences in the volatility of water and acetic acid in dilute aqueous solutions, the separation of acetic acid from water is an energy-expensive process. It is thus

desirable to develop a new separation process to save energy. The PV, EV, and TDEV techniques are potential candidates for this purpose. So far, a few articles have dealt with studies on the separation of acetic acid/water mixtures by PV with poly(acrylic acid)-grafted nylon 6,[23] poly(4-vinylpyridine-*co*-acrylonitrile),[24] charged nafion,[25] silicalite-filled poly(dimethylsiloxane),[26] and alginate composite membranes.[27] However, the separation factors were found to be low in PV in these studies.

Properties such as chemical stability, film-forming ability, and high hydrophilicity make poly(vinyl alcohol) (PVA) an attractive polymer for use as a PV membrane for the dehydration of acetic acid.[28] Because of the high hydrophilicity of PVA, the membrane must be insolubilized by modification reactions, such as crosslinking or grafting, without the loss of its hydrophilicity.

Nguyen et al.[29] prepared PVA–polybase blend membranes for the permeation of acetic acid/water mixtures, but these membranes had low separation factors.

Ksumocahyo et al.[28] crosslinked PVA thermally for PV of acetic acid/water mixtures, but they obtained low permeation rates because of crosslinking.

To improve the permeation properties of PVA membranes and obtain high-performance membranes for PV, EV, and TDEV, we grafted itaconic acid (IA) onto PVA. The PVA-*g*-IA copolymer was characterized with Fourier transform infrared (FTIR), proton nuclear magnetic resonance (¹H-NMR), and differential scanning calorimetry (DSC), and the effects of the feed composition, operating temperature, and temperature of the membrane surroundings on the performance of the membranes were investigated.

EXPERIMENTAL

Materials

PVA was purchased from Merck (Darmstadt, Germany). The molecular weight and degree of saponification were 72,000 and greater than 98%, respectively. IA was a product of Sigma Chemical Co. (Munich). Acetic acid (extra-pure-grade), cerium(IV) ammonium nitrate, and nitric acid were products from Merck and were used as received.

Graft copolymerization

The graft copolymerization of IA onto PVA was carried out in water with cerium(IV) ammonium nitrate (CeAN)/nitric acid as an initiator at 45°C for 4 h in an atmosphere of N_2. PVA (3 g) was dissolved in 50 mL of distilled water with stirring and heating to 90°C. IA (0.0462 mol) was dissolved in 25 mL of distilled water and mixed with a PVA solution. Oxygen-free nitrogen

was purged through the solution for 30 min. At this stage, 25 mL of a cerium(IV) ammonium nitrate/nitric acid ($9.12 \times 10^{-3}M/0.188M$) solution was added to the reaction mixture. After a specified time interval, the obtained polymers were precipitated out with an excess of acetone, and then the copolymer was treated with methanol to remove the poly(itaconic acid). The copolymer was washed in methanol for 2 h. The washing methanol was changed at least four times, and the washing solution was checked for the poly(itaconic acid) content. The grafted polymer was vacuum-dried at 40°C for 48 h and weighed. The graft yield of the copolymer was found to be 10 wt % ([PVA] = 30 g/L, [IA] = 0.462*M*, [CeAN] = $9.12 \times 10^{-3}M$, [HNO₃] = 0.188*M*, temperature = 45°C, time = 4 h):

$$\text{Graft yield (\%)} = \frac{(W_g - W_0)}{W_0} \times 100 \qquad (1)$$

where W_0 and W_g are the weights of the original (ungrafted) and grafted PVA, respectively.

Membrane preparation

An aqueous 5 wt % PVA-*g*-IA solution was prepared through the dissolution of preweighed quantities of dry PVA-*g*-IA in water and heated at 90°C for at least 12 h. The solution was cast onto a petri dish, and the solvent was evaporated at 30°C to form a membrane. The dried membrane was pealed off the dish and heated in a thermoset oven for 1 h at 150°C. The resulting membrane was stored in distilled water for further use. The PVA-*g*-IA membrane prepared in this research was very stable and used at least 10 times without any deformation during the PV, EV, and TDEV processes.

IR analysis

FTIR spectra of grafted and ungrafted PVA membranes were taken with a Mattson 1000 FTIR spectrometer.

DSC

The thermal analysis was performed with a Dupont General V4.1C 2000 differential scanning calorimeter. The 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 the slopes was taken as the glass-transition temperature (T_g).

Swelling measurements

The dried membrane samples were immersed in acetic acid/water mixtures of different concentrations in PV
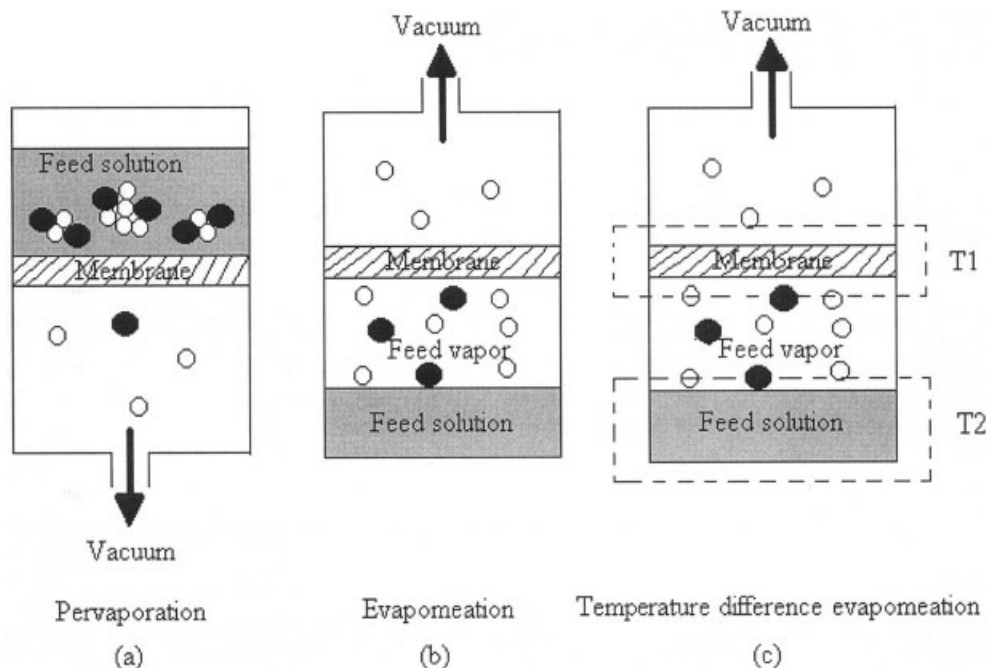
Figure 1 Principal schemes of (a) the PV method, (b) the EV method, and (c) the TDEV method.

and were exposed to a vapor of an acetic acid solution in EV at 25°C for at least 48 h. The membranes were weighed as quickly as possible, after being wiped with a cleansing tissue. Then, the samples were dried in a vacuum oven at room temperature until a constant weight was obtained. The swelling degree (SD) was calculated as follows:

$$SD = \frac{(w_s - w_d)}{w_d} \times 100 \qquad (2)$$

where w_s is the weight of the swollen membrane in the feed solution or feed vapor and w_d is the weight of the dried membrane.

PV

The PV experiments were carried out at the desired temperature (30–50°C), and the pressure at the downstream site was kept at 0.7 mbar with a vacuum pump (Edwards). The membrane area was 12.5 cm^2. The feed mixture was circulated through the cell from the feed tank, which was kept in a constant-temperature water bath. When steady-state flow conditions were reached, the permeate vapor was collected in liquid nitrogen traps and weighed. The composition of the permeate was deducted through the measurement of the refractive indices with an Atago DD-5 type digital differential refractometer.

The EV and TDEV experiments were carried out in the same way as the PV experiments.

The separation factor ($\alpha_{\text{water/acetic acid}}$) of PV, EV, and TDEV was computed as follows:

$$\alpha_{\text{water/acetic acid}} = \frac{P_{\text{water}}/P_{\text{acetic acid}}}{F_{\text{water}}/F_{\text{acetic acid}}} \qquad (3)$$

where F_{water} and $F_{\text{acetic acid}}$ and P_{water} and $P_{\text{acetic acid}}$ are the compositions (wt %) of the water and acetic acid components in the feed and permeate, respectively. For EV and TDEV, the separation factor was calculated with the vapor compositions because the membrane came into contact with the feed vapor on the feed side of the membrane (Fig. 1).

The permeation rate (kg/m^2 h) in both PV and EV was determined from the weight of the permeate collected in the cold traps, the permeation time, and the effective membrane area.

The separation index (SI) was calculated with the following equation:[17]

$$SI = J\alpha \qquad (4)$$

where J is the permeation rate.

RESULTS AND DISCUSSION

Characterization of the PVA-*g*-IA copolymer

Figures 2 and 3 show a possible reaction mechanism and IR spectra of PVA and grafted PVA films, respectively. The spectrum of grafted PVA shows a strong
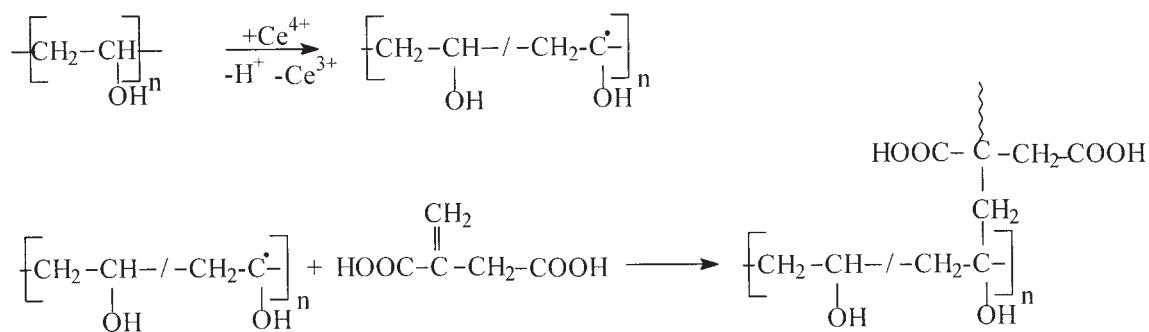
Figure 2 Postulated grafting reaction mechanism of PVA and IA.

absorption band at 1716 cm^{-1} due to the presence of the acid groups, providing substantial evidence of grafting onto PVA.[30]

T_g plays an important role in determining a membrane's performance because a high or low T_g makes a polymer tough and rubbery, and this affects the permeability of the membrane. The PVA polymer used in this study showed a T_g of 92°C, but the value for PVA-g-IA was found to be 112°C. T_g is affected by both the degree of modification and the character of the substituent, so for the PVA-g-IA copolymer, T_g increases as the bulkiness of the side chain increases, and the presence of the carboxylic group imparts less

rotational freedom to the side chain, resulting in a higher T_g in grafted PVA.

Figure 4 shows the ^{1}H-NMR spectrum of PVA-g-IA. A signal centered at 9.5 ppm, due to the carboxylic proton of IA, can be observed. A similar result is reported in the literature.[31] Gimenez et al.[31] modified PVA with carboxylic acid anhydrides and reported signals at 11.5 ppm due to the carboxylic proton.

Effect of the feed composition in PV

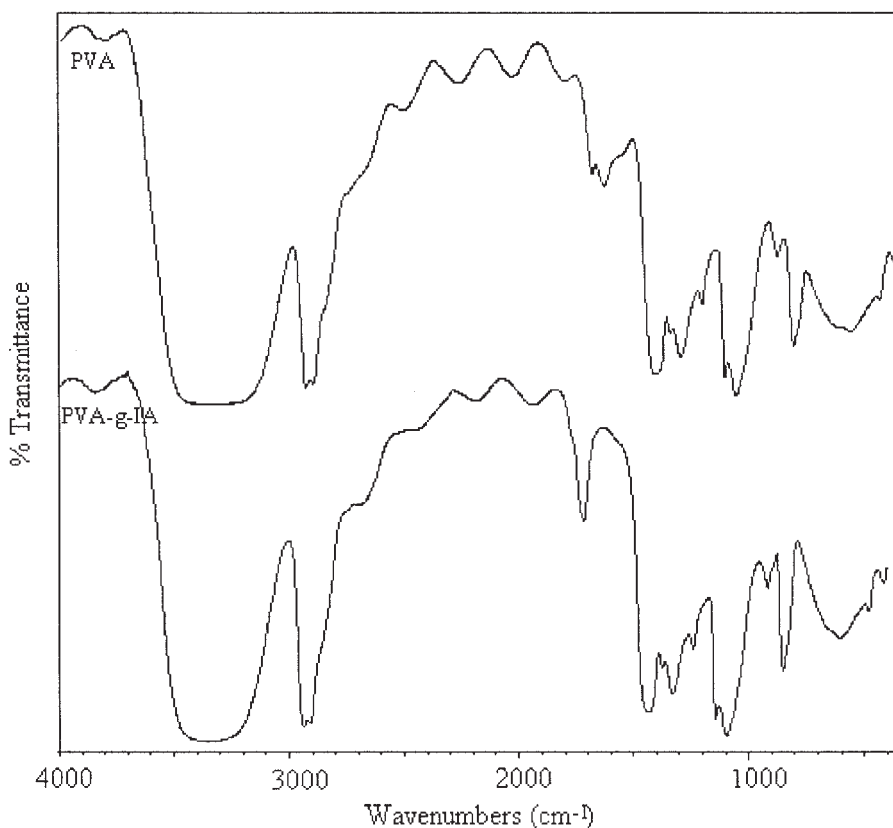Figures 5 and 6 show the effect of the feed composition on the PV performance of membranes. Both the

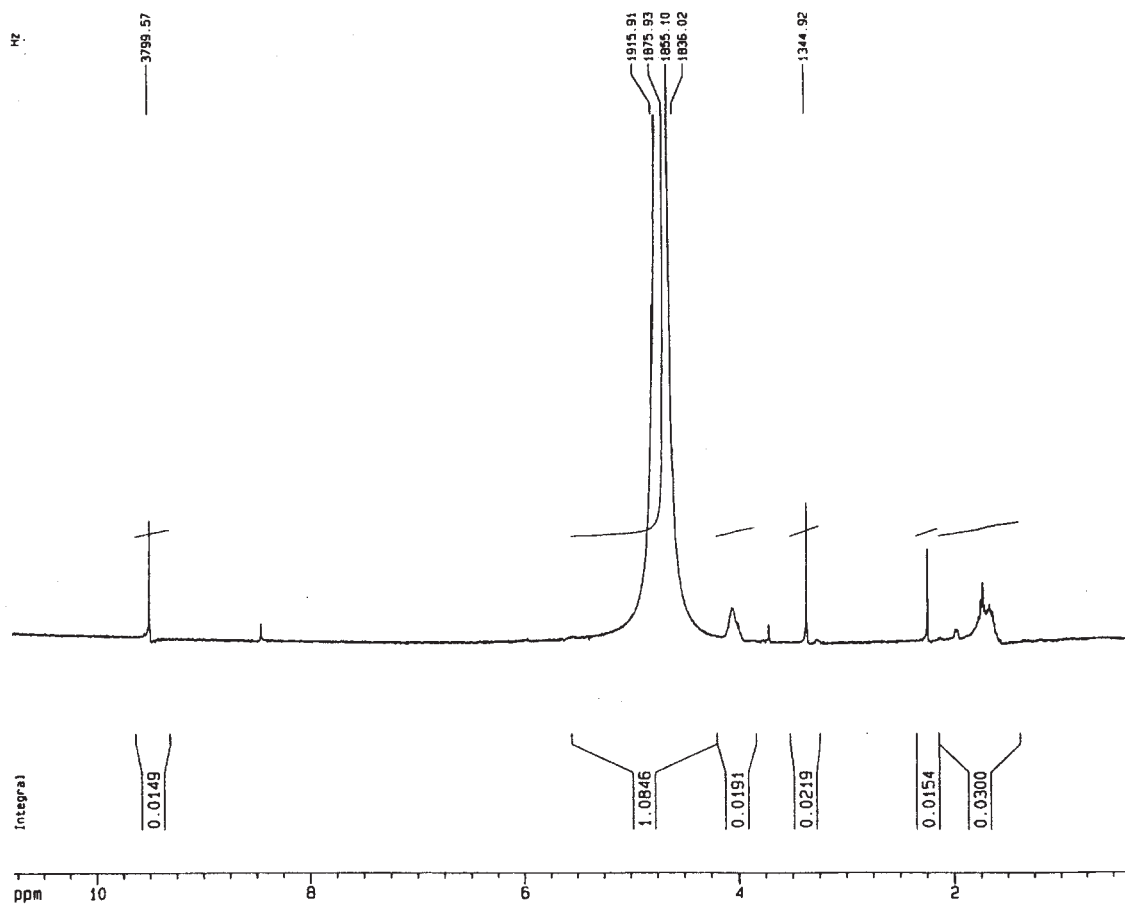**Figure 3** IR spectra of PVA and PVA-g-IA membranes.

Figure 4 ^{1}H-NMR spectrum of an IA-grafted PVA polymer.

permeation rates and separation factors for the PVA-g-IA membrane were better than those for the PVA membrane. Free carboxylic acid groups in the grafted PVA are believed to have increased the hydrogen-bonding interaction with the water molecules. Hence, the permeation and separation characteristics of the grafted membrane were enhanced with the copolymerization. The PV separation of acetic acid/water
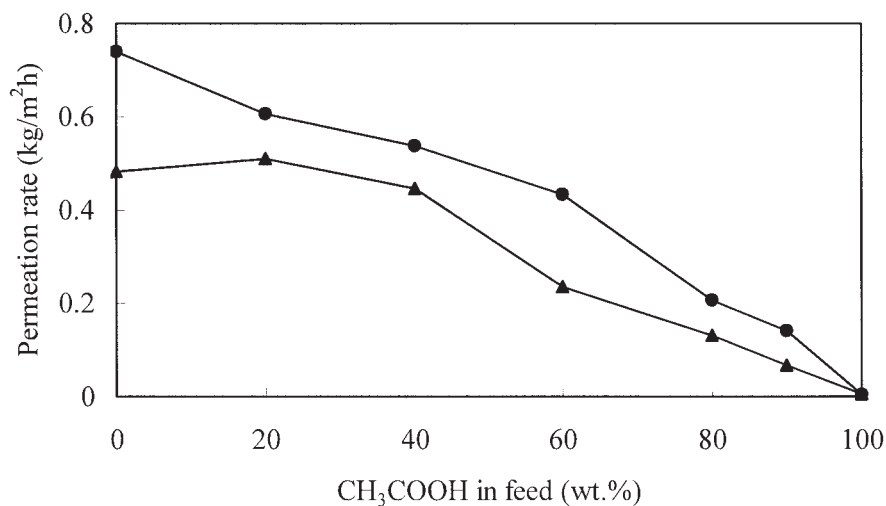

Figure 5 Variation of the permeation rate with the feed composition in (▲) PVA and (●) PVA-g-IA. The permeation conditions were as follows: membrane thickness = 80 μm, operation temperature = 40°C, and pressure = 0.7 mbar.
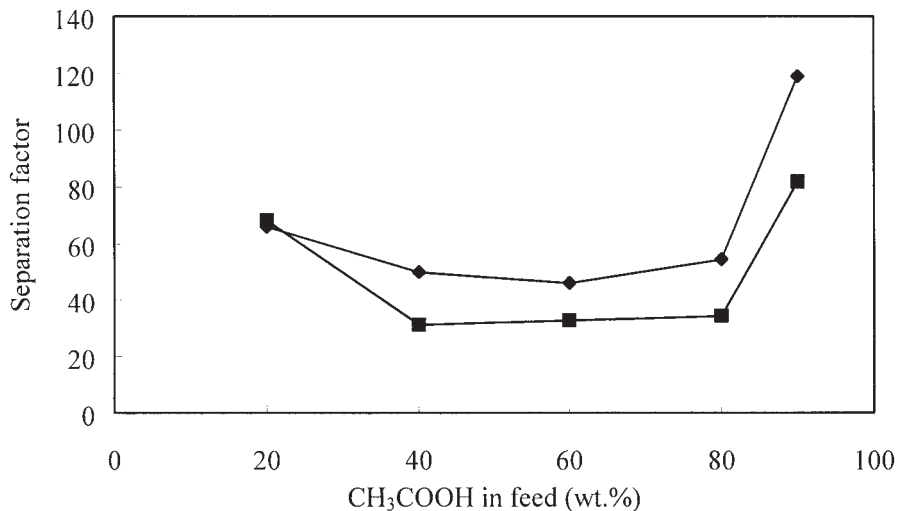
Figure 6 Variation of the separation factor with the feed composition in (■) PVA and (♦) PVA-*g*-IA. The permeation conditions were as follows: membrane thickness = 80 μm, operation temperature = 40°C, and pressure = 0.7 mbar.

mixtures was carried out over a range of 20–90 wt % acetic acid in the feed at 40°C. The separation factor and permeation rate were 66–119 and 0.005–0.740 kg/m^2 h, respectively, depending on the feed composition with the PVA-*g*-IA membrane. The permeation rate decreased monotonously with the acetic acid content in the feed, and the separation factor had a minimum value at an acetic acid concentration of about 60 wt %. At a high acetic acid concentration, because of the association of acetic acid molecules, the separation factor toward water increased. The decrease in the permeation rate with decreasing water content in the feed was due to a decrease in the selective interaction between the water molecules and the hydrophilic membranes.

Details on this were obtained through an analysis of the permeation rate data shown in Figure 7. The water permeation rate of the membrane was much higher than the acetic acid permeation rate. The water permeation rate decreased with the acetic acid content as the total permeation rate did. The acetic acid permeation rate had a maximum value around 60 wt %; that is, a permeation enhancement of acetic acid was found. This phenomenon can be explained in terms of the plasticization effect of water on the membrane.[32] The plasticization action of water enhanced the acetic acid permeation by reducing the energy required for the diffusive transport of acetic acid through the membrane, but the plasticizing effect of acetic acid for enhancing water permeation was not as remarkable as
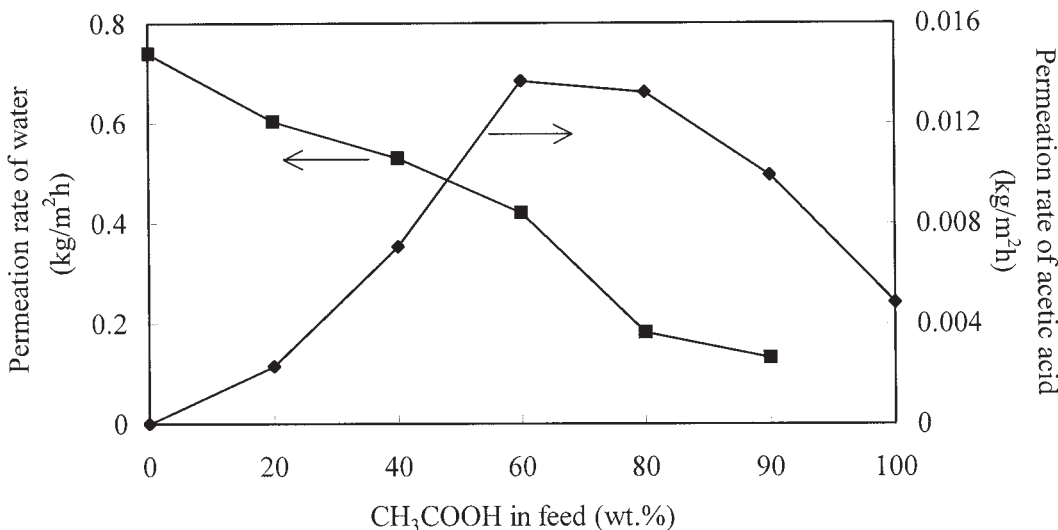

Figure 7 Variation of the permeation rate of water and acetic acid with the feed composition.
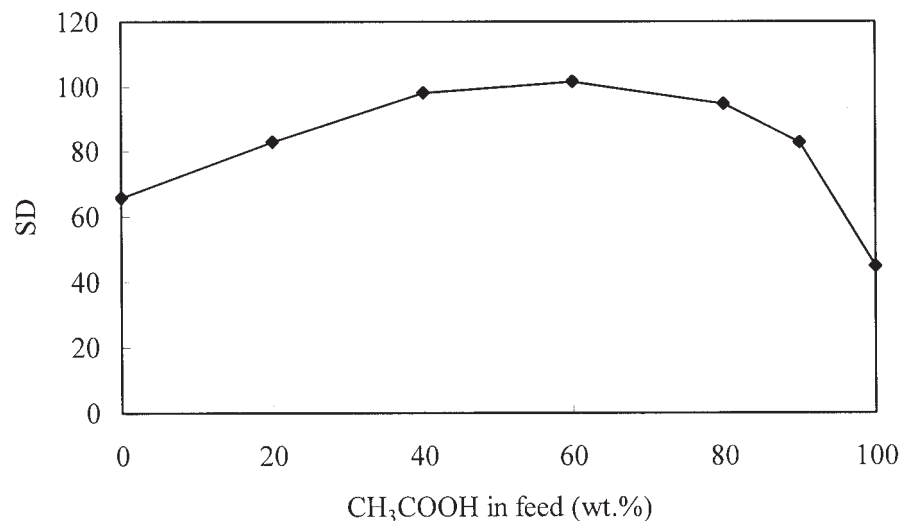
Figure 8   Change in the SD with the feed composition.

that of water; this resulted in a separation factor with a minimum value for this feed composition.

The permeation studies were also supported by swelling measurements of the membranes, which are presented in Figure 8. The swelling of the PVA-g-IA membrane increased up to an acetic acid concentration of 60 wt % because of the plasticizing action of water on the membrane and then decreased because the plasticizing action of acetic acid was less than that of water. Similar results concerning the effect of the feed composition on the PV performance have been reported in the literature.[32–35]

Yeom and Lee[32] studied the PV separation of acetic acid/water mixtures through PVA membranes crosslinked with glutaraldehyde. They concluded that the permeation rate decreased with the acetic acid content, whereas the separation factor first decreased (70–80 wt % acetic acid) and then increased with the acetic acid content.

In our previous study[34] on the separation of acetic acid/water mixtures with modified PVA membranes with malic acid, we found that in the range of 20–90 wt % acetic acid, the separation factor decreased to a minimum at 60 wt % and then increased sharply, whereas the permeation rate decreased continuously.

Huang and Yeom[35] investigated the PV separation of acetic acid/water mixtures with crosslinked PVA membranes. They observed that the separation factor decreased between 10 and 70 wt % acetic acid and then increased up to 90 wt % acetic acid, whereas the permeation rate decreased continuously.

Effect of the operating temperature in PV

Figure 9 presents the effect of the operating temperature on the permeation rate and separation factor of a grafted PVA membrane in a 20 wt % acetic acid solu-

tion. As expected, when the temperature was increased, the total permeation rate increased, but the separation factor decreased. Similar trends are also reported in the literature.[2,3,35–37] These results can be explained with the free-volume theory.

According to the free-volume theory, the thermal motion of polymer chains in the amorphous regions randomly produces free volume.[35] As the temperature rises, the frequency and amplitude of chain jumping increase, and the diffusion rate of individual permeating molecules are high, so that the total permeation rates increase and the separation factors decrease. Also, the mobility of the permeating molecules increases, and hydrogen-bonding interaction between the membrane and each component in the feed mixture decreases, as the operating temperature increases. As a result, the permeation rate increases and the separation factor toward water decreases.

Lee et al.[14] investigated the PV separation of binary organic and aqueous liquid mixtures with crosslinked PVA membranes. They observed that the permeation rates increased as the operating temperature increased and decreased as the poly(acrylic acid) (PAA) content increased in the resulting membrane.

Ruckenstein and Liang[38] prepared PVA–polyacrylamide interpenetrating polymer network membranes unsupported and supported on poly(ether sulfone) ultrafiltration membranes and investigated the permeation characteristics of water–ethanol mixtures by PV. They found that the permeation rate increased as the feed temperature increased, but the separation factor decreased.

The temperature dependence of the permeation can be expressed by an Arrhenius relationship.[38–41] Figure 10 shows Arrhenius plots of the permeation rates for 20 wt % acetic acid solutions, and the overall activa-
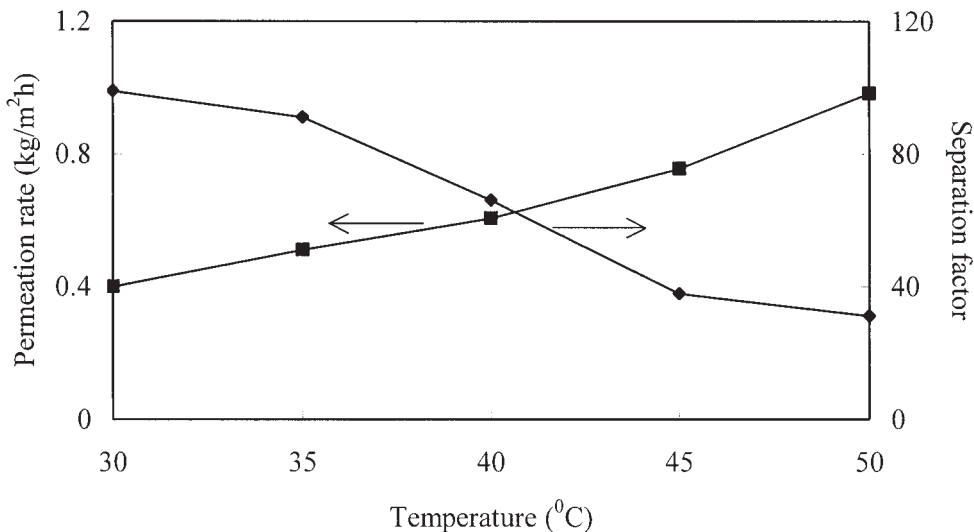
Figure 9 Change in the permeation rate and separation factor with the operation temperature. The permeation conditions were as follows: [CH$_3$COOH] = 20 wt %, membrane thickness = 80 μm, and pressure = 0.7 mbar.

tion energy of permeation was calculated to be 8.5 kcal/mol for a PVA-g-IA membrane.

Effect of the feed composition in EV

The performance of a PVA-g-IA membrane in an aqueous acetic acid solution by EV is shown in Figure 11. The permeation rate decreased with increasing acetic acid concentration in the feed vapor because of decreasing water content with acetic acid concentrations of 20–90 wt %. However, the separation factor decreased up to an acetic acid concentration of 40 wt % and then increased sharply. To explain this, we investigated the changes in the SD of grafted membranes with the acetic acid content (vapor; Fig. 12). The SD increased up to an acetic acid concentration of

40 wt % because of the plasticization action of the vapor and then decreased sharply. Through the swelling of the membrane, acetic acid molecules easily dissolved and were diffusive; this led to the minimum value for the separation for this composition.

Lai et al.[42] investigated the grafting of vinyl acetate onto a nylon-4 membrane with γ-ray irradiation for PV and EV processes. They observed that with an increase in the ethanol concentration in the feed, the permeation rate decreased, but the separation factor increased.

Effect of the operating temperature in EV

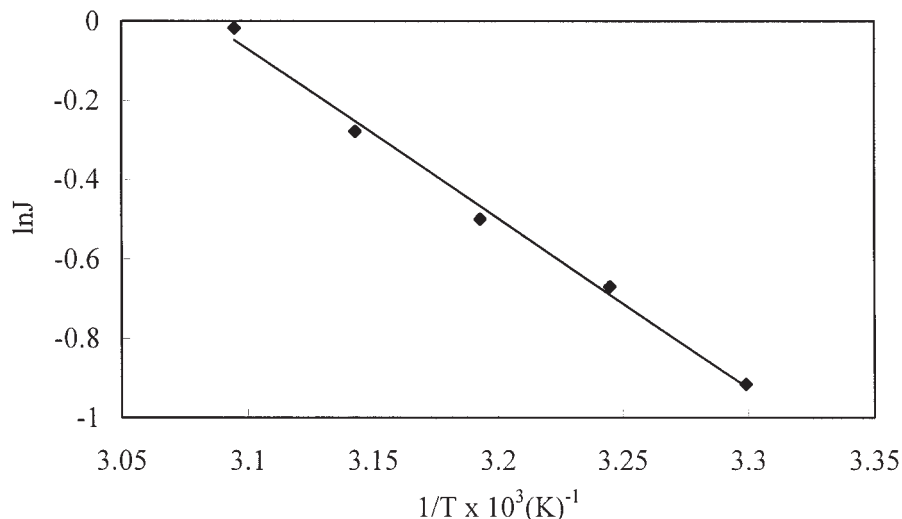The effect of the permeation temperature on the total permeation rate and separation factor for an aqueous

Figure 10 Arrhenius plot of ln J versus 1/T for a PVA-g-IA membrane in PV.
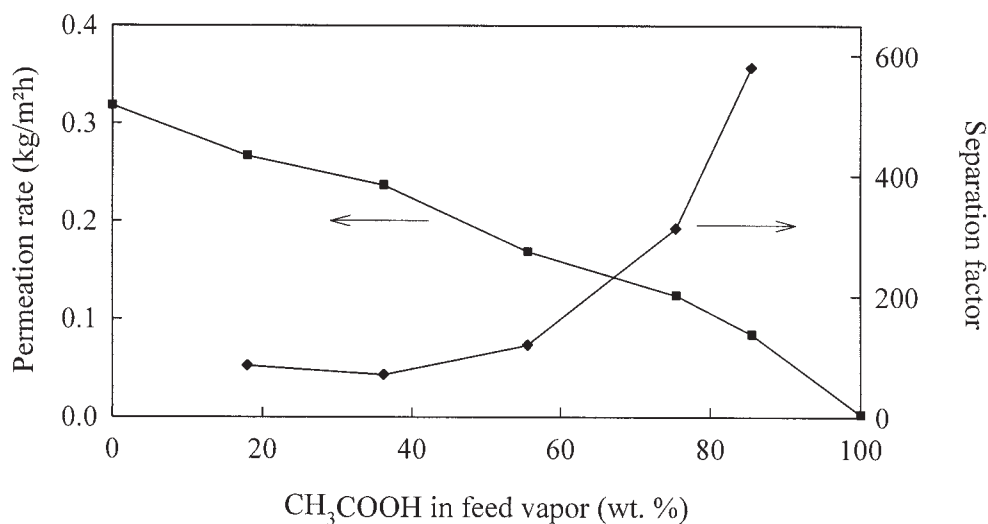
Figure 11 Variation of the permeation rate and separation factor with the feed vapor composition in EV. The permeation conditions were as follows: membrane thickness = 80 μm, operation temperature = 40°C, and pressure = 0.7 mbar.

solution of 20 wt % acetic acid in EV is shown in Figure 13; the temperatures of both the feed solution and membrane surroundings were equal. The permeation rates increased as the operating temperature increased, but the separation factors decreased as expected.[43]

Figure 14 shows that the permeation rate was inversely proportional to the absolute temperature, indicating that the experimental results agreed very well with the Arrhenius equation in EV too. The overall activation energy of permeation was calculated to be 10.2 kcal/mol.

The permeation activation energy was greater in EV than in PV. This result can be explained as follows. In EV, the membrane is not directly touched by the feed solution. The SD of the membrane in EV is less than

that in PV. Thus, the membrane has a dense structure and has greater activation energy for sorption and diffusion.

Effect of the temperature difference between the feed solution and membrane surroundings in membrane permeation

The EV method that can be controlled by a temperature difference between the feed solution and the membrane surroundings is called TDEV.[7] A basic scheme of the TDEV method is shown in Figure 1(c); the temperature of the membrane surroundings is controlled by a cold medium in a permeation cell of a jacket type. Figure 15 shows the characteristics of permeation and separation for aqueous acetic acid solu-
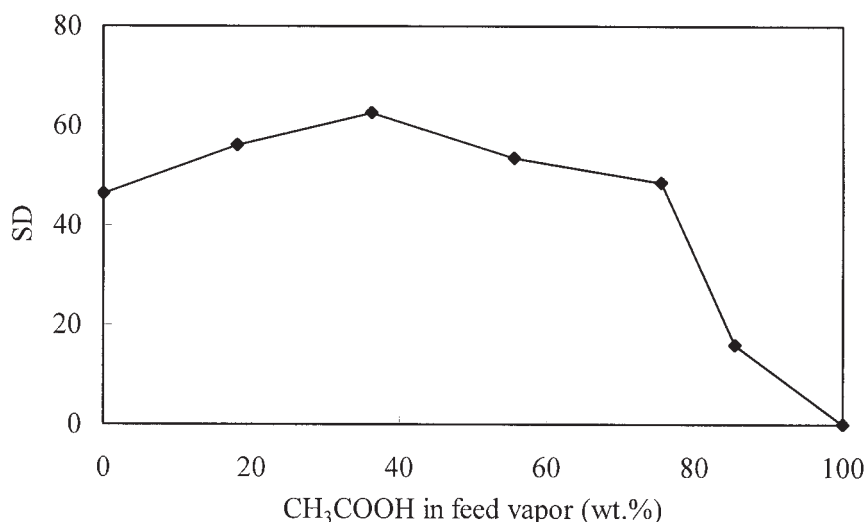

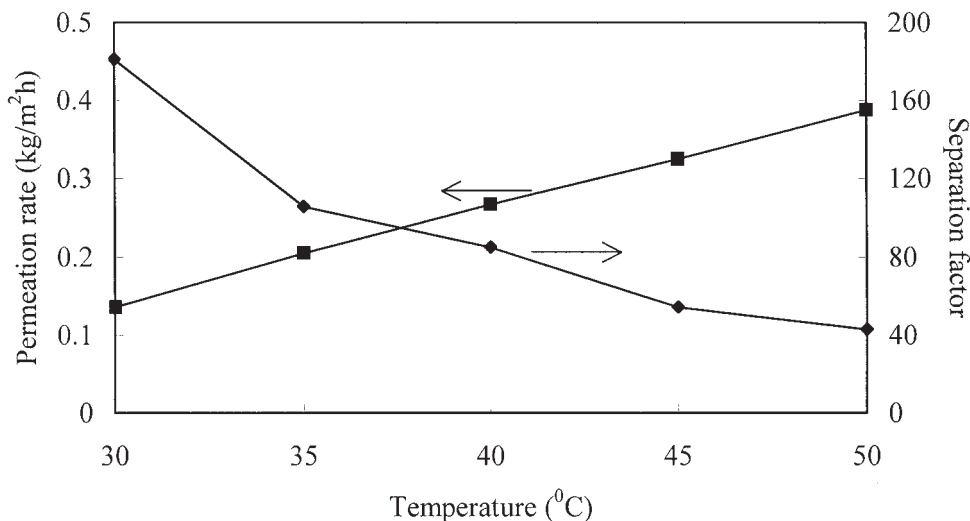**Figure 12** Change in the SD with the feed vapor composition.

Figure 13 Change in the permeation rate and separation factor with the operation temperature in EV. The permeation conditions were as follows: [CH$_3$COOH] = 20 wt %, membrane thickness = 80 μm, and pressure = 0.7 mbar.

tions through the PVA-g-IA membrane with this method. The feed was an aqueous solution of 20 wt % acetic acid, the temperature of the feed solution was kept constant at 40°C, and the temperature of the membrane surroundings was changed to a temperature lower than the temperature of the feed solution. The permeation rate decreased but the separation factor toward water increased with a lowering of the temperature of the membrane surroundings. The decrease in the permeation rate was attributable to the decrease in the motion of the permeating molecules and polymer chains comprising the membrane with a reduction of the temperature of the membrane surroundings. On the other hand, as the temperature of the membrane surroundings decreased, vaporized

acetic acid molecules aggregated more than water molecules (because the freezing points of acetic acid and water were 16.7 and 0°C, respectively). It was very difficult for these aggregated acetic acid molecules to be incorporated into the PVA-g-IA membrane and be diffused through this membrane.

This aggregation of acetic acid molecules was responsible for the increase in the separation factor toward water through the grafted membrane. In addition, the increase in the separation factor may have been due to the increase in the solubility of the water vapor in the hydrophilic membrane with a drop in the temperature of the membrane surroundings according to Henry's law. Similar results have been reported in the literature.[44–46]
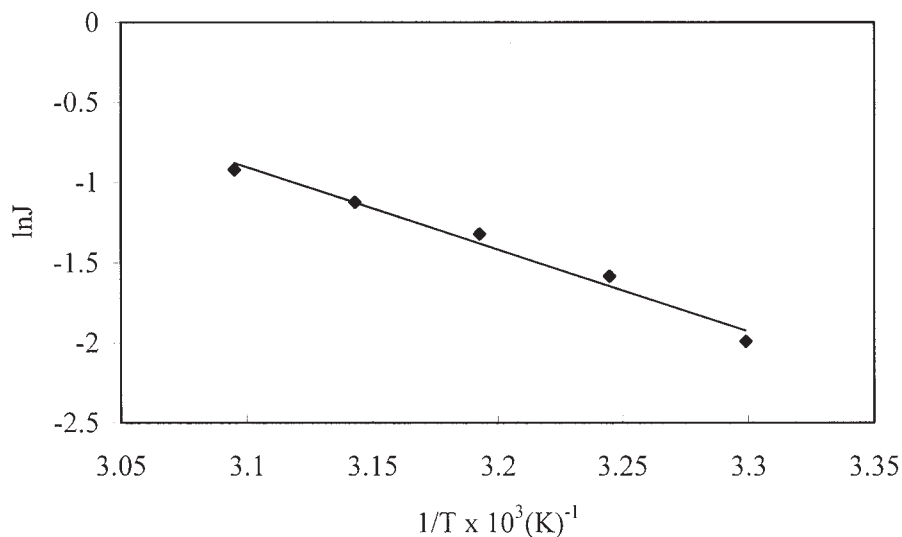

Figure 14 Arrhenius plot of ln J versus $1/T$ for a PVA-g-IA membrane in EV.
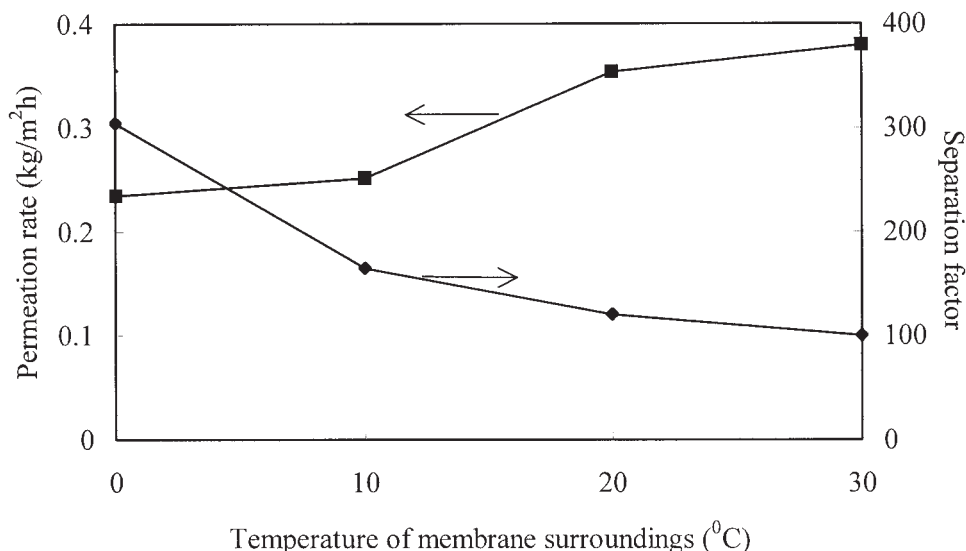
Figure 15 Effect of the temperature of the membrane surroundings on the permeation rate and separation factor. The permeation conditions were as follows: $[CH_3COOH]$ = 20 wt %, membrane thickness = 80 μm, temperature of the feed solution = 40°C, and pressure = 0.7 mbar.

Uragami and Shinomiya[45] investigated the permeation characteristics of chitosan membranes with TDEV. They observed that both the total permeation rate and separation factor increased as the temperature of the membrane surroundings decreased.

Uragami[46] researched the separation of aqueous and organic liquid solutions through chitosan, poly-(vinyl chloride), and poly(dimethylsiloxane) membranes. He observed that when the temperature of the feed solution was kept constant in TDEV and the temperature of the membrane surroundings was changed, permselectivity for water increased in chitosan and poly(vinyl chloride) membranes; however, in poly(dimethylsiloxane) membranes, the permselectivity for ethanol increased when the temperature of the membrane surroundings decreased.

Comparison of the permeation and separation characteristics with the PV, EV, and TDEV methods

The effects of the acetic acid concentration in the feed solution or feed vapor on the total permeation rate

and separation factor through a PVA-g-IA membrane with each method are shown in Table I; the feed temperature was set at 40°C for PV, EV, and TDEV, and the temperature of the membrane surroundings was 20°C. The permeation rates followed the order of PV > TDEV > EV, whereas the separation factors were in the order of TDEV > EV > PV.

Water predominantly permeated through the grafted membrane with each method because of the hydrophilicity and smaller molecular size. The permeation rates decreased with an increase in the acetic acid concentration in the feed solution with the three methods. However, the permeation rate with EV was lower than that with PV. These results might be due to the fact that the membranes were in direct contact with the feed solution and were more swollen with PV than with EV and TDEV. Thus, the diffusivity of the permeating species during the diffusion process in EV was lower. Furthermore, the separation factors of the PVA-g-IA membranes with EV and TDEV were higher than those of the membrane with PV. The separation factor and permeation rate with the TDEV method

TABLE I
Changes in α, J, and SI with the Acetic Acid Concentration for Each Method

Acetic acid in the feed (wt %)	PV			EV			TDEV		
	α	J (kg/m^2 h)	SI (kg/m^2 h)	α	J (kg/m^2 h)	SI (kg/m^2 h)	α	J (kg/m^2 h)	SI (kg/m^2 h)
20	66.1	0.607	40.1	85.1	0.267	22.7	120.1	0.354	42.5
40	50.0	0.537	26.9	70.2	0.237	16.6	105.5	0.308	32.5
60	46.0	0.434	20.0	119.2	0.169	20.1	126.0	0.260	32.7
80	54.6	0.207	11.3	313.0	0.124	38.8	368.0	0.197	72.5
90	118.8	0.141	16.8	580.0	0.084	48.7	686.0	0.144	98.8

were higher than those of EV because of the temperature difference between the feed mixture and the membrane surroundings. Table I also compares the three methods with respect to the SI value. The highest SI was obtained with TDEV at acetic acid concentrations of 20–90 wt %. Hence, it could be concluded that TDEV was better for separating aqueous acetic acid solutions than PV and EV with PVA-*g*-IA membranes.

CONCLUSIONS

The following conclusions were drawn from this study:

1. Grafting IA onto PVA improved the performance (i.e., permeation rate and separation factor) of the PVA membranes.
2. Increasing the operating temperature in PV and EV increased the permeation rate and reduced the separation factor in the temperature range of 30–50°C. The activation energies in PV and EV were calculated to be 8.5 and 10.2 kcal/mol, respectively.
3. In the separation of aqueous acetic acid solutions with concentrations of 20–90 wt %, the permeation rates followed the order of PV > TDEV > EV, whereas separation factors were in the order of TDEV > EV > PV.
4. The TDEV method was more suitable for the separation of acetic acid/water mixtures, especially at high acetic acid concentrations.

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