

# Separation Characteristics of Acetic Acid–Water Mixtures Using Poly(vinyl alcohol-*g*-4-vinyl pyridine) Membranes by Pervaporation and Temperature Difference Evapomeation Techniques

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**ABSTRACT:** The separation of acetic acid–water mixtures was carried out using pervaporation (PV) and temperature difference evapomeation (TDEV) methods. For the separation process, 4-vinyl pyridine was grafted on poly(vinyl alcohol). Membranes were prepared from the graft-copolymer by casting method and crosslinked by heat treatment. The effects of feed composition on the separation characteristics were studied and the performances of the separation methods were compared. Permeation rates were

found to be high in PV whereas separation factors were high in TDEV method. Membranes gave permeation rates of 0.1–3.0 kg/m<sup>2</sup>h and separation factors of 2.0–61.0 depending on the composition of the feed mixture and the method. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1385–1394, 2006

**Key words:** separation techniques; membranes; graft copolymers; pervaporation; evapomeation

## INTRODUCTION

Pervaporation is an energy efficient and environmentally clean process used to separate desired components in aqueous organic, close boiling, or azeotropic mixtures with energy saving.<sup>1–8</sup> It is used commonly in chemical, food, and pharmaceutical industries to concentrate heat-sensitive products, in analytical applications, to enrich a given component for quantitative detection, and for environmental problems, to remove volatile organic contaminants from waste water.<sup>9</sup>

This technique differs from other separation processes in that the membrane behaves as a barrier between a liquid in the liquid phase and the permeate in the vapor phase.<sup>10</sup> In this process liquid–feed mixture is in direct contact with the membrane in the upstream and the permeate is removed from the downstream as a vapor.<sup>11</sup> Although PV is an attractive method for the separation processes, it has several disadvantages such as swelling or shrinking of the membrane, which causes a decrease in selectivity because of the direct contact of feed solution with the membrane material.<sup>7–13</sup> A new method called Evapomeation (EV) was developed for the elimination of such disadvantages.<sup>5,7,12,14–18</sup>

The disadvantages of PV could be suppressed in EV because the feed solution is not in direct contact with the membrane material and only the feed vapor contacts to the membrane. For improving the membrane performance in the permeation and separation of aqueous organic mixtures, temperature of the feed solution and the membrane neighborhood can be controlled. This newer and more effective EV method that establishes a temperature difference between the feed solution and membrane surroundings is called as Temperature Difference-Controlled Evapomeation Method (TDEV).<sup>5,14,16–18</sup> So far few studies have dealt with the separation processes using TDEV, and most of them focused on the aqueous alcohol systems.

Uragami and Morikawa<sup>5</sup> studied the separation of alcohol–water mixtures by using poly(dimethyl siloxane) membranes. They observed higher permeabilities and selectivities for ethanol solutions in TDEV method than in EV and PV techniques.

Uragami and Shinomiya<sup>16</sup> used PV, EV, and TDEV techniques to concentrate aqueous alcoholic solutions through modified silicone rubber membrane and they concluded that TDEV method is the powerful method to develop a higher selectivity in the membrane separation.

Uragami and Shinomiya<sup>14</sup> also tried to concentrate aqueous dimethyl sulfoxide solutions through a chitosan membrane by PV, EV, and TDEV methods. They found that TDEV method was more effective than the other methods.

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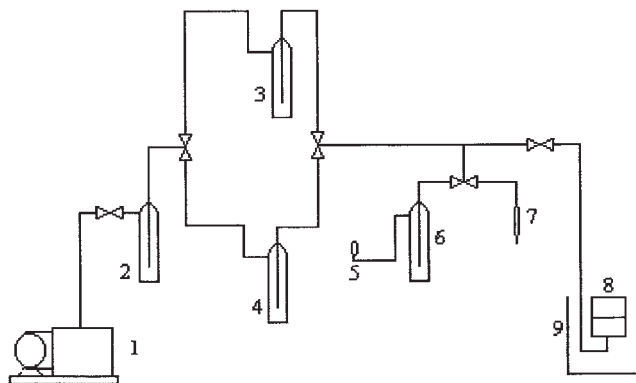
Uragami<sup>18</sup> have also studied the separation of aqueous organic solutions (aqueous dimethyl sulfoxide, acetic acid, and ethanol) by using some polymeric membranes as (poly(vinyl chloride), chitosan, poly(dimethyl siloxane)) with TDEV method. He reported that when the temperature of the feed solution was kept constant while changing the temperature of the membrane surroundings, permselectivity for water was facilitated.

In membrane separation processes, the choice of polymeric material depends on the type of application. For the separation of aqueous organic mixtures, the membrane should be water-selective and must have hydrophilic substrates so that the membrane allows water to permeate easily.<sup>19</sup> Poly(vinyl alcohol) (PVA) is a suitable polymer for the dehydration processes because of its good chemical stability, film-forming ability, and high hydrophilicity except for its poor stability in water. To overcome this problem, PVA must be insolublized. However this process loses the hydrophilic character of PVA. To increase the hydrophilicity of PVA, the processes such as blending,<sup>11,20–25</sup> crosslinking,<sup>1,10,26–28</sup> grafting<sup>3,29–31</sup> etc., are usually carried on in the presence of hydrophilic polymers.

A Lewis base 4-vinyl pyridine (4VP) is an attractive material to improve the hydrophilic character of the water-permselective membranes.<sup>19,32</sup> Chen and Lai<sup>19</sup> grafted 4-vinyl pyridine onto polycarbonate (PC) to prepare water-permselective membrane to separate water–ethanol mixtures by pervaporation. They reported that the higher hydrophilicity of the grafted membrane facilitates the water transport through the grafted membrane better than through the unmodified membrane and they concluded that grafting 4VP on to the PC membrane not only improves the separation factor but also increases the permeation rate in the separation of water–ethanol mixtures. Lee and Oh<sup>33</sup> prepared polyacrylonitrile (PAN) membranes by copolymerizing acrylonitrile with 4-vinyl pyridine to form an in situ complex between the pyridine moiety in the membrane and the carboxylic acid in the feed for the separation of acetic acid–water mixtures by PV.

Acetic acid is an important chemical commodity, which is often contaminated with aqueous waste/recycling streams from chemical process industries.<sup>31</sup> Separation of acetic acid from water by normal binary distillation is difficult because of low relative volatility; thus, for the separation of acetic acid–water mixtures more energy-intensive and expensive azeotropic distillation or sometimes solvent extraction is used.<sup>34</sup> Studies related to the separation of acetic acid–water mixtures mostly based on PV method<sup>31,35–50</sup> but few studies have dealt with TDEV method.<sup>18,51–52</sup>

In this study, 4-vinyl pyridine was grafted on PVA and membranes prepared from the synthesized poly(vinyl alcohol-g-4 vinyl pyridine) (PVA-g-4VP) co-



**Figure 1** Schematic diagram of the apparatus used in PV and TDEV experiments. (1: vacuum pump, 2–4,6: permeation traps, 5: McLeod manometer, 7: vent, 8: permeation cell, and 9: constant temperature water bath)

polymer to separate acetic acid–water mixtures by PV and newer efficient evapomeation method, TDEV.

## EXPERIMENTAL

### Materials

PVA (MW: 72,000, degree of saponification > 98%) and acetic acid were provided by Merck Chemicals, UK. PAA (MW: 2000) and 4-Vinyl Pyridine were purchased from sigma-Aldrich, Germany.

### Apparatus and measurements

The apparatus used in PV and TDEV experiments is illustrated in Figure 1.

The permeation cells were assembled from two half cells made of glass. They were connected together by joints. The capacity of each cell was about 150 mL. Membranes were placed on to the porous glass support. The effective area of the membrane was 12.5 cm<sup>2</sup>. Feed liquid was poured into the upstream side of the cell and downstream side was vacuumed in the case of pervaporation [Fig. 2(a)] and experiments were carried out under a reduced pressure of 1.5 mbar (Vacuu Brand RD 15. GMBH Lab, Germany). Permeated vapor was collected in liquid nitrogen traps and the composition of the permeate was analyzed by using digital refractometer (Atago Differential Refractometer DD-5, Atago, Japan).

For TDEV experiments, feed solution was poured into the downstream side of the cell and vacuum was applied to the upstream side of the TDEV cell [Fig. 2(b)] and the temperature of the feed solution was kept different from that of the membrane surrounding.

Performance of the membranes were expressed as separation factor ( $\alpha$ ), permeation rate ( $Q$ ), and pervaporation separation index (PSI). The separation factor

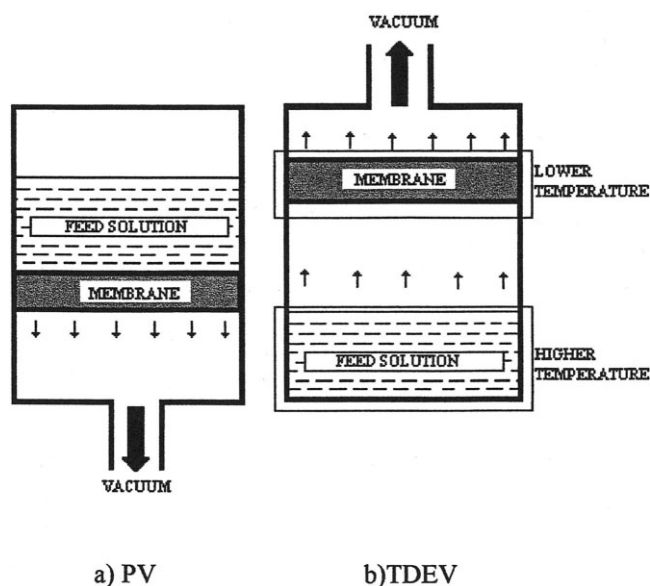


Figure 2 Schematic representations of (a) PV (b) TDEV.

based on the composition of feed solution and permeate was calculated as follows:

$$\alpha = \frac{Y_{\text{H}_2\text{O}}/Y_{\text{CH}_3\text{COOH}}}{X_{\text{H}_2\text{O}}/X_{\text{CH}_3\text{COOH}}} \quad (1)$$

where  $X_{\text{H}_2\text{O}}$ ,  $X_{\text{CH}_3\text{COOH}}$ ,  $Y_{\text{H}_2\text{O}}$ , and  $Y_{\text{CH}_3\text{COOH}}$  denote the weight fractions of water and acetic acid in the feed and in the permeate respectively, for PV.

The separation factor for TDEV based on the compositions of feed vapor and permeate was calculated by using

$$\alpha = \frac{Y_{\text{H}_2\text{O}}/Y_{\text{CH}_3\text{COOH}}}{V_{\text{H}_2\text{O}}/V_{\text{CH}_3\text{COOH}}} \quad (2)$$

where  $V_{\text{H}_2\text{O}}$  and  $V_{\text{CH}_3\text{COOH}}$  represents the weight fractions of water and acetic acid vapor from the feed solution.  $Y_{\text{H}_2\text{O}}$  and  $Y_{\text{CH}_3\text{COOH}}$  denote the weight fractions of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{COOH}$  in the permeate respectively.

The permeation rate,  $Q$  was determined by using the equation

$$Q = \frac{M}{At} \quad (3)$$

where  $M$ ,  $A$ , and  $t$  denotes the weight of the permeate (kg), effective membrane area ( $\text{m}^2$ ), and operating time (h) respectively.

Pervaporation separation index, PSI was calculated using the equation

$$\text{PSI} = Q\alpha \quad (4)$$

In which  $Q$  and  $\alpha$  are the permeation rate and separation factor respectively.

In the pervaporation of binary mixtures, the actual permeation rate deviates from the ideal rate because of plasticization action of the permeants and the interaction between permeants and the polymer.<sup>27</sup> So a permeation ratio,  $\theta$ , has been defined to explain the deviation of the actual permeation rate ( $Q$ ) from the ideal rate, ( $Q^0$ ) and it was calculated by the following equation<sup>27,28</sup>:

$$\theta = Q/Q^0 \quad (5)$$

For the ideal binary liquid mixtures, the permeation rate for each component can be given as

$$q_i^0 = X_i Q_i^0 \quad (6)$$

$$q_j^0 = X_j Q_j^0 \quad (7)$$

$$Q^0 = q_i^0 + q_j^0 \quad (8)$$

where  $i$  and  $j$  denote the individual components in the binary mixture,  $X$  is the weight fraction in the feed mixture, superscript "0" denotes ideal permeation.<sup>28</sup> The permeation ratio for each component can be expressed as

$$\theta_i = q_i/q_i^0 \quad (9)$$

$$\theta_j = q_j/q_j^0 \quad (10)$$

where  $q_i$  and  $q_j$  are the actual permeation rates of individual components and

$$Q = q_i + q_j \quad (11)$$

Swelling degrees, SD, of the membranes were computed by using

$$\text{SD} = \frac{W - W_0}{W_0} \quad (12)$$

where  $W$  and  $W_0$  are the wet and dry masses of the membranes respectively.

### Synthesis of PVA-g-4VP copolymer

PVA (3.0 g) was dissolved in 100 mL distilled water, and 8.5 mL 4VP (distilled) was added to the polymer solution and they were both put into a three-necked round bottom flask equipped with a magnetic stirrer, thermometer, and  $\text{N}_2$  inlet. Then the flask was placed in a constant temperature bath at  $50^\circ\text{C}$ . After the addition of 0.08 g of  $\text{Bz}_2\text{O}_2$ , polymerization reaction was carried out for 2 h. At the end of this period, grafted

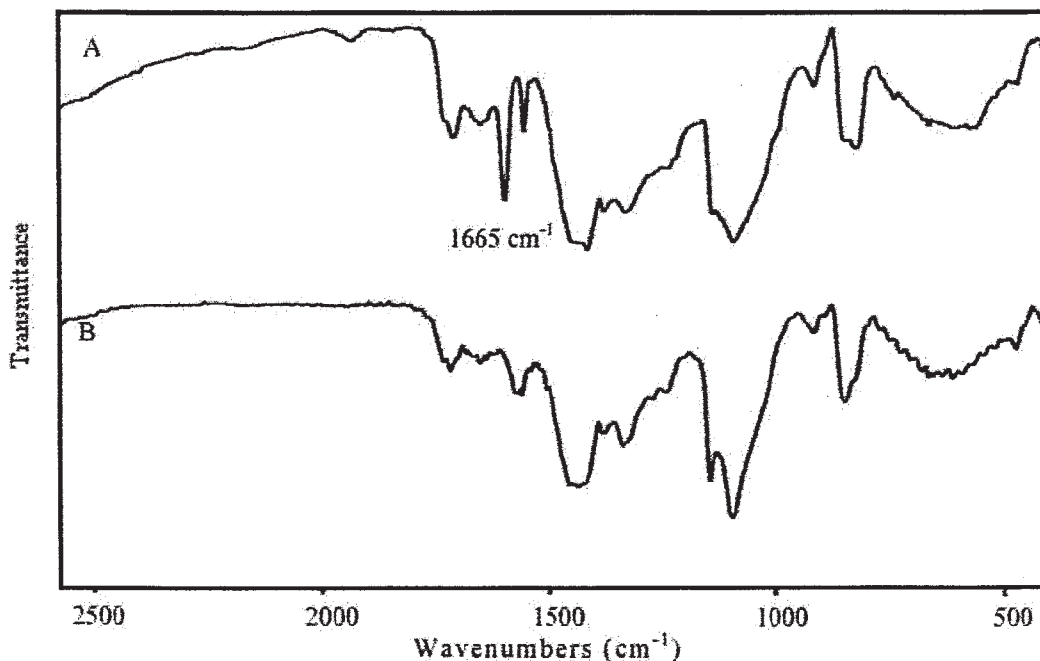


Figure 3 FTIR spectrum for (A)PVA-g-4VP (B) PVA membranes.

copolymer was precipitated in an excess amount of acetone and washed with methanol and tetrahydrofuran to remove the homopolymer. The characteristic pyridine peak was observed at  $1600\text{--}1665\text{cm}^{-1}$  in the FTIR spectrum of the graft copolymer<sup>33</sup> (PVA-g-4VP) (Fig. 3) and the grafting percentage was found to be 29% from the elemental analysis of PVA-g-4VP.

#### Preparation of PVA-g-4VP membranes

PVA-g-4VP membranes were prepared by using the 5% (m/v) solution of copolymer in 50% (v/v) ethanol-water mixture. Definite amount of prepared polymer solution were taken into the petri dishes (4.5 cm in diameter). They were dried at  $35^{\circ}\text{C}$  till to complete dryness and heat-treated at  $150^{\circ}\text{C}$  for 1 h. The prepared membranes were preserved in distilled water till to use. The thickness of the membranes was found to be  $50\ \mu\text{m}$  by micrometer (Sigma-Aldrich Co., Germany).

#### Swelling measurements

Swelling studies were carried out by immersing PVA-g-4VP membranes in acetic acid-water solutions at different concentrations (0–100 wt %) to determine the wet masses. After drying the membranes the masses of dry membranes were determined. The SD values of PVA-g-4VP membranes were calculated by using eq. (12).

## RESULTS AND DISCUSSION

#### Separation of acetic acid-water mixtures using PV method

The effect of concentration of feed mixture on permeation rate and separation factor was studied at  $40^{\circ}\text{C}$  temperature and 1.5 mbar pressure<sup>50</sup> with PVA-g-4VP membranes by using PV method and the results were given in Figure 4.

As it can be seen from the Figure 4, first permeation rate increased then decreased as the amount of acetic acid in the feed increased. This can be explained by the catalytic transfer mechanism. According to this mechanism in situ complex ions were formed between the pyridine moiety in the membrane and the incoming acetic acid from the feed.<sup>33</sup> The acetic acid-pyridine complex was determined from the FTIR spectrum of PVA-g-4VP membranes (Fig. 5) that had been dipped to the acetic acid-water solutions of 60 wt % and 80 wt % for complex formation. As it is seen from the spectrum that the characteristic pyridine peaks at  $1600\text{--}1665\text{cm}^{-1}$  disappeared and a new carbonyl peak representing the complex formation appeared at  $1718\text{cm}^{-1}$ .

The complex between pyridine and acetic acid attracts water molecules through ion-dipole interactions at the surface of the membrane, and then these water molecules were transported easily to the other side of the membrane. As the amount of acetic acid in the feed is increased the permeation rate gets lower because of the lower content of water in the feed

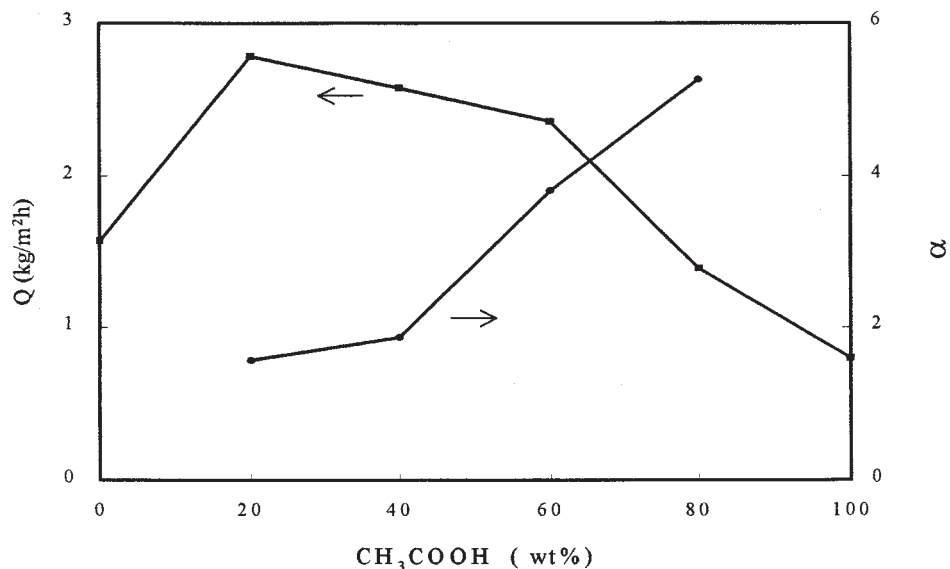


Figure 4 The change of permeation rate and separation factor with the feed composition by using PV method. ■  $Q$ ; ●  $\alpha$

mixture. When the water content in the feed mixture increases, greater amount of water attracted to the membrane surface by the in situ complex of pyridine-acetic acid and this causes a plastization effect on the membrane material, therefore the separability of the membrane material for water decreases because of the additional transfer of acetic acid molecules through the swollen membrane as it is seen from the Figure 4.

In Figure 6, SD values of PVA-g-4VP membranes for different acetic acid concentrations were given. As it is seen from the figure, SD values that were obtained in the presence of acetic acid-water mixture were higher

than that of the pure acetic acid and pure water because of the in situ complex formation between the acetic acid molecules and pyridine groups of the membrane, as explained above.

From the swelling studies, it was also determined that SD for PVA and PVA-g-4VP membranes were found to be 35 wt % and 81 wt % in water respectively. This means that 4VP increases the hydrophilic character of the PVA membranes. Similar results were obtained by the study of Chen and Lai.<sup>19</sup> They have prepared 4-vinylpyridine-homografted-polycarbonate (PC-g-4VP) copolymer membrane in the separation of ethanol-water mixtures by using PV and concluded

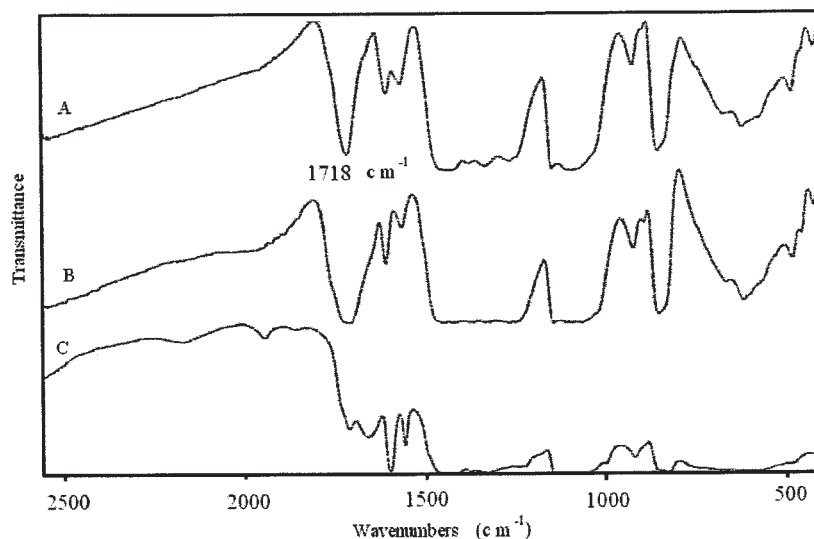


Figure 5 FTIR spectrum of PVA-g-4VP membranes corresponding to the complex formation of pyridine and acetic acid. (A) PVA-g-4VP membranes dipped into CH<sub>3</sub>COOH (80 wt %), (B) PVA-g-4VP membranes dipped into CH<sub>3</sub>COOH (60 wt %), (C) PVA-g-4VP

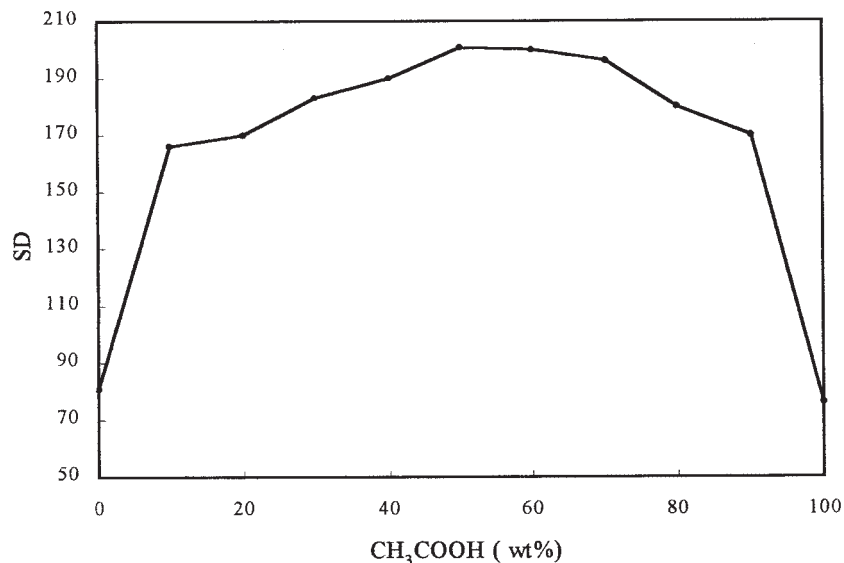


Figure 6 The change of SD with the feed composition for PVA-g-4VP membranes.

that as the percentages of 4VP increases in the copolymer, the SD values of the membranes increases because of the high hydrophilic character of 4VP groups.

Figure 7 shows the comparison of the individual permeation rates of acetic acid and water with the total permeation rate. As it is given in the figure, the permeation rate of water shows the same tendency as the total permeation rate and it was very close to the total permeation rate curve. This means that PVA-g-4VP membranes transfer water preferentially than acetic acid. Similar results can also be seen from the McCabe diagrams (Fig. 8) that PVA-g-4VP membranes give greater interest toward water than acetic acid for the acetic acid–water systems.

In the pervaporation of two component systems, the effect of the one component on the transfer of the other component can be given by permeation ratio, which is simply the deviation of the permeation rates of the components from the ideal behavior. Interaction between the permeants and membrane material effects the permeation performance of the membrane.<sup>47</sup> When the system exhibits an ideal permeation behavior, the permeation ratio should be equal to unity. When  $\theta > 1$  the interactions between polymer and permeants give a positive effect on permeation and when  $\theta < 1$  the interactions effect the permeation negatively.<sup>27,28</sup> The permeation ratios of the acetic acid–water system was calculated by using eqs. (9) and

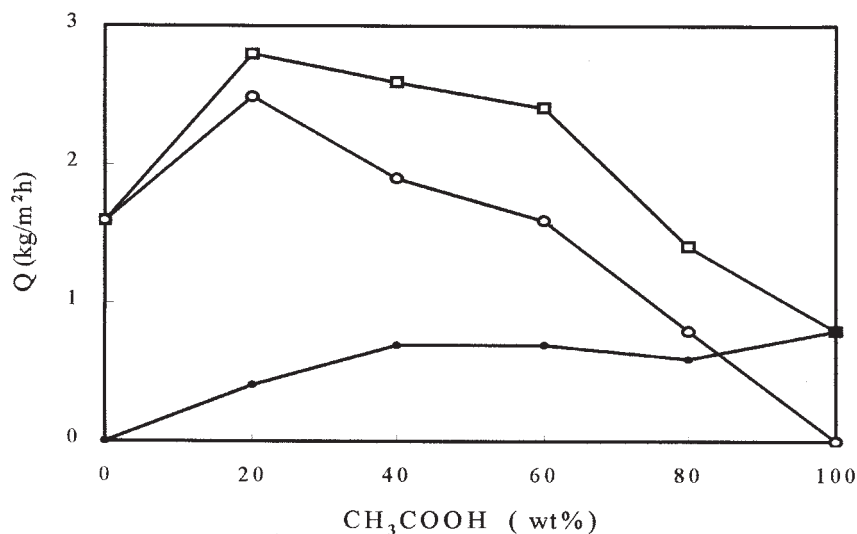


Figure 7 Comparison of the permeation rates of acetic acid and water with the total permeation rate. □ Q (total); ● Q (CH<sub>3</sub>COOH); ○ Q (H<sub>2</sub>O)

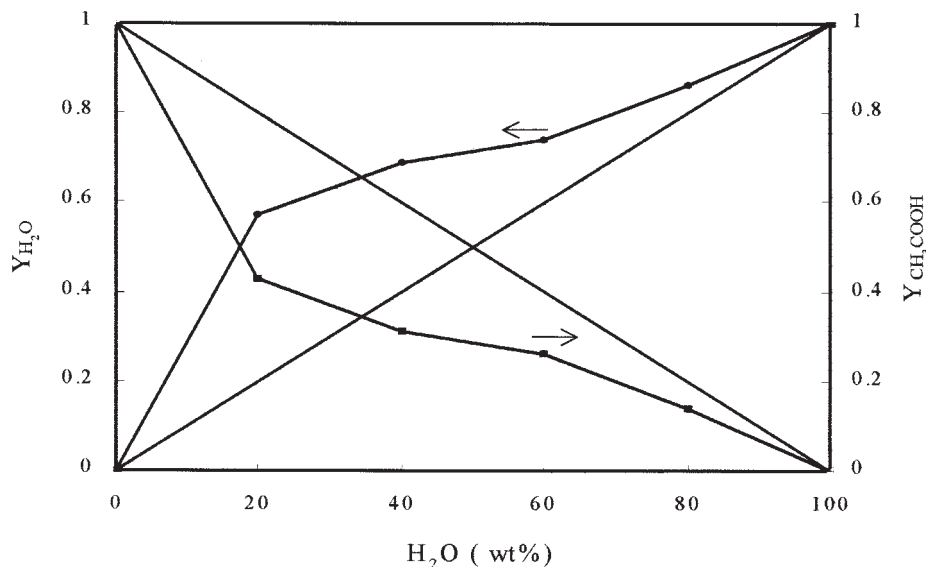


Figure 8 McCabe diagrams of acetic acid and water in the pervaporate for PV. ●Y (H<sub>2</sub>O); ■Y(CH<sub>3</sub>COOH).

(10) and the results were presented in Figure 9. As it is seen from the figure that,  $\theta$  values of the feed solution and the components are all greater than unity, which means that the presence of one component had affected the permeation behavior of the other positively.

Pervaporation separation index values were calculated by using eq. (4) and are presented in Figure 10. As it is reflected from the figure performance of PVA-g-4VP membranes are good at higher acetic acid concentrations in PV.

**Separation of acetic acid- water mixtures using TDEV method**

TDEV method was also used in the separation of acetic acid–water mixtures. The effect of feed compo-

sition on the permeation rate and separation factor was studied. The temperature of the feed solution was kept at 40°C and membrane surrounding was allowed to the room temperature. The results obtained from the permeation studies were given in Figure 11. It is clearly appear that as the amount of acetic acid increases both the flux and separation factor decreases.

In the case of TDEV method membrane is not in direct contact with feed mixture therefore the swelling effect of the feed mixture is not so great as in the case of pervaporation. So the molecular size of the permeating molecules becomes very important to characterize the permeation behavior. It is known that acetic acid has greater molecular size (0.40 nm) than water molecules (0.28 nm). As the amount of acetic acid

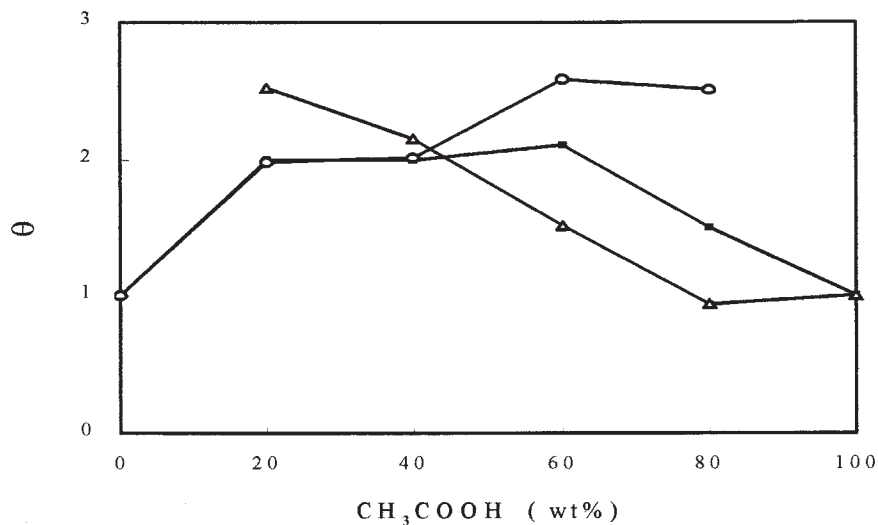


Figure 9 Change of permeation ratios with the composition of the feed mixture. Δ Acetic acid; o Water; ■ Feed solution.

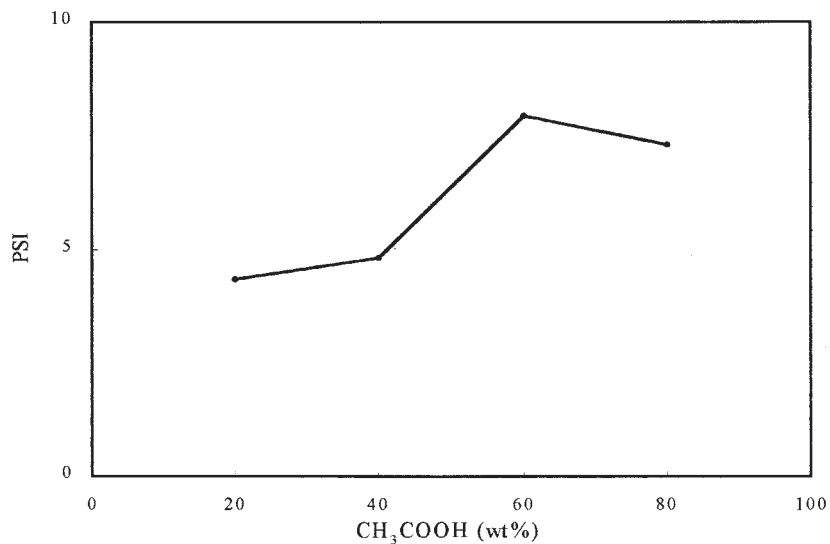


Figure 10 Pervaporation separation index values for PVA-g-4VP membranes.

increases in the feed mixture, it becomes difficult for acetic acid molecules, which are present in a greater amount at high acid concentrations, to diffuse through the less swollen membrane so the permeation rate decreases. Additionally when the acetic acid and water which had been vaporized from the feed mixture come close to the membrane surrounding, acetic acid vapor aggregates much easier than the water vapor because the freezing point of acetic acid is greater than that of water (16°C and 0°C respectively). This aggregation of acetic acid molecules is responsible for the permselectivity for water through PVA-g-4VP membranes. The compound which is present in the vapor phase in a greater amount with a greater vapor pressure at 40°C (the vapor pres-

ures of water and acetic acid are 55.3 mmHg and 34.4 mmHg respectively, at 40°C) will dissolve in the membrane material, which has lower temperature than the feed mixture, according to the Henry's Law, which states that the solubility of gases are greater at lower temperatures. Therefore, as the acetic acid content of the feed solution increases in the feed solution, the amount of acetic acid molecules in the vapor phase and in the aggregated form increase. Because of the swelling effect of the acetic acid on the membrane material as explained previously, acetic acid molecules permeates through the swollen membrane as well as the water molecules, so the separation factor decreases too.

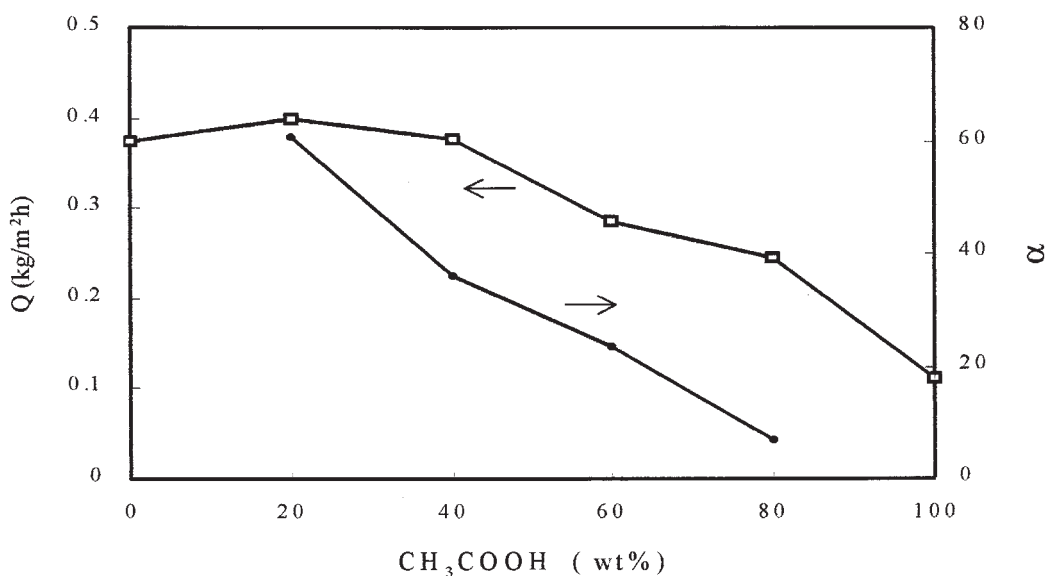


Figure 11 The variation of permeation rates and separation factors of PVA-g-4VP membranes with the feed composition by using TDEV method. □ Q; ● α



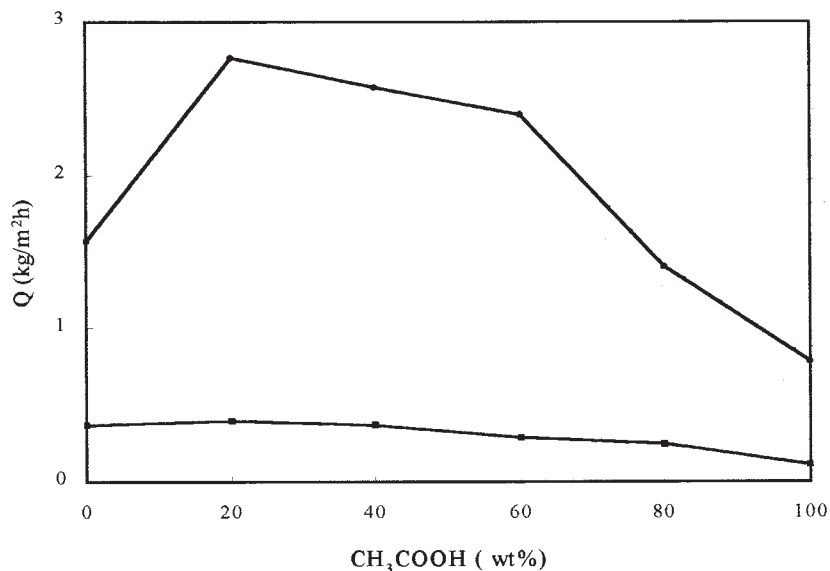


Figure 12 Comparison of permeation rates of PVA-g-4VP membranes. ● PV; ■ TDEV.

Uragami<sup>18</sup> obtained similar results in the separation of aqueous dimethyl sulfoxide and acetic acid solutions using chitosan, poly(vinyl chloride) and poly(dimethyl siloxane) membranes.

In Figures 12 and 13 the permeation rates and separation factors obtained in PV and TDEV methods by using PVA-g-4VP membranes were compared. As it was reflected from the figures that permeation rates were high in PV method, whereas separation factors were high in TDEV method.

= 76.6°C).<sup>53</sup> It was separated by using PVA-g-4VP membranes in TDEV method: the temperature of the membrane surrounding was kept at the room temperature 40°C. The separation factor and permeation rate were determined as 21.0 and  $36.40 \times 10^{-2}$  kg/m<sup>2</sup>h respectively. This means that the azeotropic mixture of acetic acid and water can be separated by a percentage of 95 wt % by using TDEV method with PVA-g-4VP membranes.

#### Separation of acetic acid-water azeotropic mixtures by using TDEV method

Acetic acid forms an azeotropic mixture with water at a concentration of 3 wt % of CH<sub>3</sub>COOH ( $T_b$

#### CONCLUSIONS

In the present study 4VP was grafted on PVA then membranes were prepared from the grafted copolymer and the prepared membranes were used in

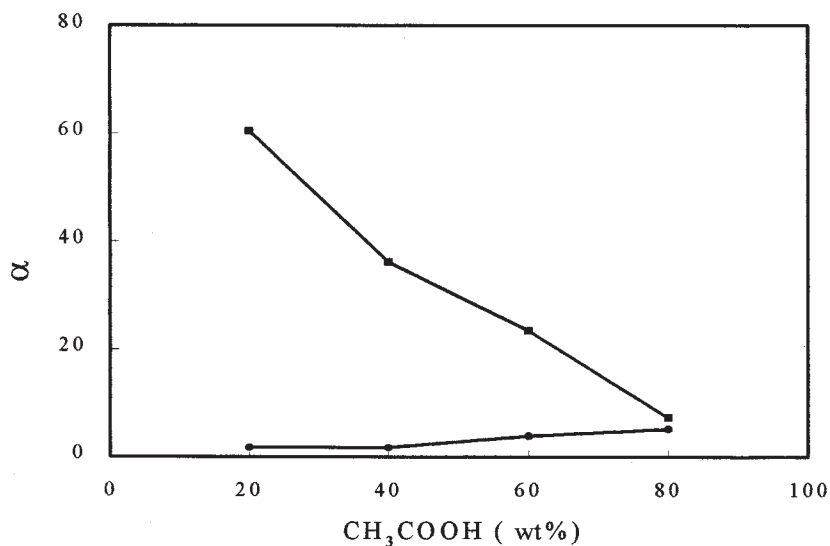


Figure 13 Comparison of the separation factors of PVA-g-4VP membranes in PV and TDEV methods. ● PV; ■ TDEV.

the separation of acetic acid water mixtures by using PV and TDEV methods.

By this study it was determined that grafting 4VP onto PVA, increases the hydrophilic character of PVA membranes. Additionally formation of an in situ complex between the acetic acid and 4VP enhances the permeation behavior of the PVA-g-4VP membranes while decreasing the separability toward water molecules at high water content in the feed solution. PVA-g-4VP membranes gave permeation rates of 0.80–2.80 kg/m<sup>2</sup>h and separation factors 2.0–5.0 depending on the feed composition in PV.

By using TDEV method greater separation factors (7.0–61.0) were determined while the permeation rates (0.10–0.40 kg/m<sup>2</sup>h) get lower than that obtained in PV. Azeotropic mixture of acetic acid and water can be separated by a percentage of 95.0 wt % in TDEV with separation factor of 21.0 and permeation rate of  $36.40 \times 10^{-2}$  kg/m<sup>2</sup>h.

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