Separation Characteristics of Acetic Acid–Water Mixtures by 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 by 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 effect of feed composition on the separation characteristics was studied and the performances of the separation methods were compared. Permeation rates obtained in PV were found to be high, whereas separation factors were high in TDEV method. Membranes gave permeation rates of 0.1–3.0 kg/(m² 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: 2030–2039, 2006

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

INTRODUCTION

Pervaporation (PV) is an energy efficient and environmentally clean process used to separate selectively desired components in aqueous organic, close boiling, or azeotropic mixtures with energy saving.[1–8] 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, and to remove volatile organic contaminants from waste water.[9]

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.[10] 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.[11] 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.[7–13] A new method called evapomeation (EV) was developed for the improvement of such disadvantages.[5,7,12,14–18] 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 with 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).[5,14,16–18] So far a few articles have dealt with the studies on separation processes using TDEV and most of them focused on the aqueous alcohol systems.

Uragami and Morikawa[5] 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 EV and PV techniques.

Uragami and Shinomiya[16] 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[14] 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.

Uragami[18] has also studied the separation of aqueous organic solutions (aqueous dimethyl sulfoxide, acetic acid, and ethanol) by using some polymeric membranes (poly(vinyl chloride), chitosan, and 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.[19] 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,[11,20–25] crosslinking,[1,10,26–28] grafting,[3,29–31] 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.[19,32] Chen and Lai[19] grafted 4-vinyl pyridine onto polycarbonate (PC) to prepare water-permselective membrane to separate water–ethanol mixtures by PV. 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[33] prepared polyacrylonitrile 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.[31] Separation of acetic acid from water by normal binary distillation is difficult due to 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.[34] Studies related to the separation of acetic acid–water mixtures mostly based on PV method,[31,35–50] but a few articles have dealt with TDEV method.[18,51–52]

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) copol-
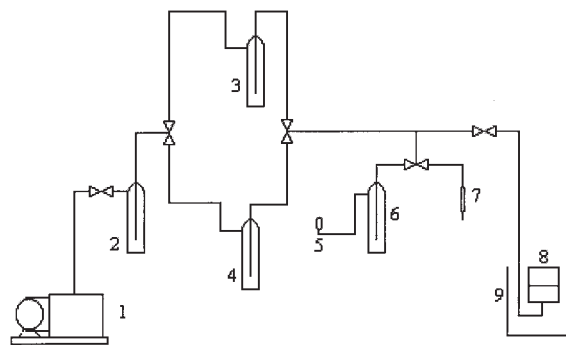

Figure 1 Schematic diagram of the apparatus used in PV and TDEV experiments. ((1) vacuum pump, (2–4, 6) permeation traps, (5) Mc Leod manometer, (7) vent, (8) permeation cell, and (9) constant temperature water bath).

ymer to separate acetic acid–water mixtures by PV and newer-efficient EV 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 onto the porous glass support. The effective area of the membrane was 12.5 cm². Feed liquid was poured into the upstream side of the cell and the downstream side was vacuumed in the case of PV [Fig. 2(a)] and experiments were carried out under a reduced pressure of 1.5 mbar (Vacuu Brand RD 15, GMBH Co. Lab., Germany). Permeated vapor was collected in liquid nitrogen traps and the composition of permeate was analyzed by using a 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 surroundings.

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

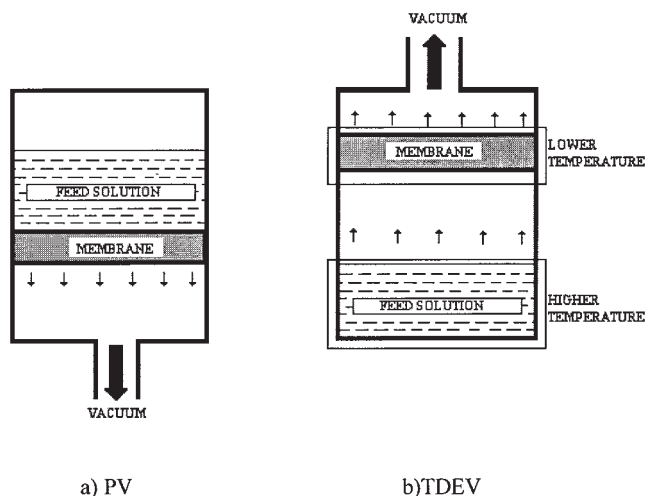a) PV   b)TDEV

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

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

$$\alpha = \frac{Y_{H_2O}/Y_{CH_3COOH}}{X_{H_2O}/X_{CH_3COOH}} \qquad (1)$$

where X_{H_2O}, X_{CH_3COOH}, Y_{H_2O}, and Y_{CH_3COOH} denote the weight fractions of water and acetic acid in the feed and in the permeate, respectively, for PV.

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

$$\alpha = \frac{Y_{H_2O}/Y_{CH_3COOH}}{V_{H_2O}/V_{CH_3COOH}} \qquad (2)$$

where V_{H_2O} and V_{CH_3COOH} represents the weight fractions of water and acetic acid vapor from the feed solution. Y_{H_2O} and Y_{CH_3COOH} denote the weight fractions of H_2O and CH_3COOH in the permeate, respectively.

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

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

where M, A, and t denote the weight of the permeate (kg), effective membrane area (m²), and operating time (h), respectively.

PSI was calculated using the equation

$$PSI = Q\alpha \qquad (4)$$

in which Q and α are the permeation rate and separation factor, respectively.

In the PV 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.[27] So a permeation ratio, θ, has been defined to explain the deviation of the actual permeation rate (Q) from the ideal rate (Q^o), and it was calculated by the following equation:[27,28]

$$\theta = Q/Q^o \qquad (5)$$

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

$$q_i^o = X_i\,Q_i^o \qquad (6)$$

$$q_j^o = X_j Q_j^o \qquad (7)$$

$$Q^o = q_i^o + q_j^o \qquad (8)$$

where i and j denote the individual components in the binary mixture, X is the weight fraction in the feed mixture, and the superscript "o" denotes ideal permeation.[28] The permeation ratio for each component can be expressed as

$$\theta_i = q_i/q_i^o \qquad (9)$$

$$\theta_j = q_j/q_j^o \qquad (10)$$

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

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

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

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

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

Synthesis of PVA-_g_-4VP copolymer

Three grams of PVA 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-bottomed flask equipped with a magnetic stirrer, thermometer, and N_2 inlet. Then the flask was placed in a constant temperature bath at 50°C. After the addition of 0.08 g of Bz_2O_2, a polymerization reaction was carried out for 2 h. At the end of this period, grafted copolymer was precipitated in an excess amount of acetone and washed with methanol and tetrahydrofuran to remove the homopolymer. The
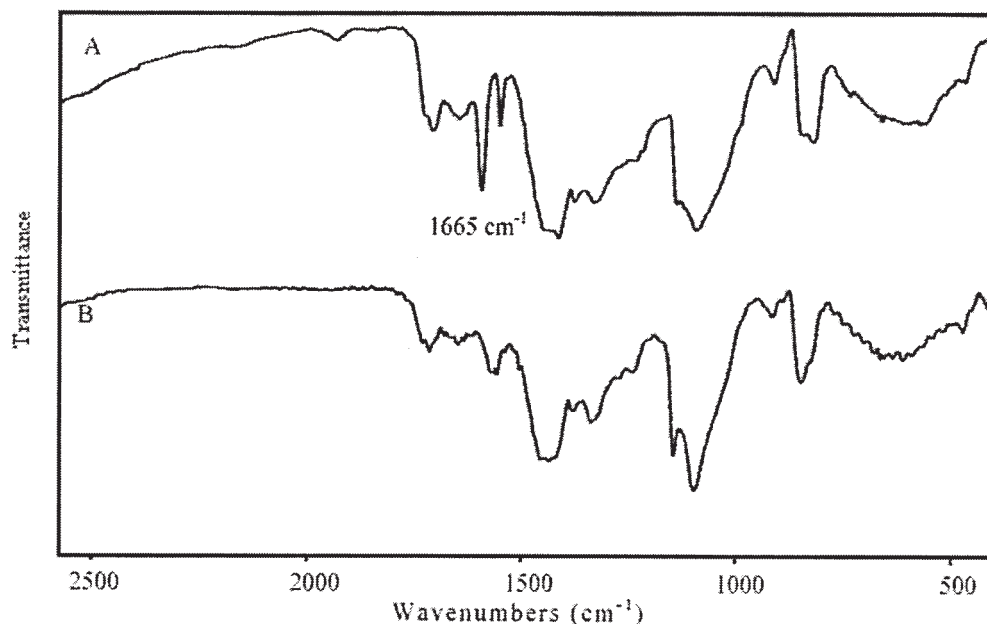
Figure 3 FTIR spectrum for (a) PVA-*g*-4VP and (b) PVA membranes.

characteristic pyridine peak was observed at 1600–1665 cm^{-1} in the FTIR spectrum of the graft copolymer[33] (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°C till complete dryness and heat-treated at 150°C for 1 h. The prepared membranes were preserved in distilled water till use. The thickness of the membranes was found to be 50 μm by micrometer (Sigma–Aldrich, 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°C temperature and 1.5 mbar pressure[50] 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, initially the 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.[33] The acetic acid–pyridine complex was determined from the FTIR spectrum of PVA-*g*-4VP membranes (Fig. 5) that had been dipped in the acetic acid–water solutions of 60 and 80 wt % for complex formation. As it is seen from the spectrum, the characteristic pyridine peaks at 1600–1665 cm^{-1} disappeared and a new carbonyl peak representing the complex formation appeared at 1718 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 mixture. When the water content in the feed mixture increases, greater amount of water was 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.
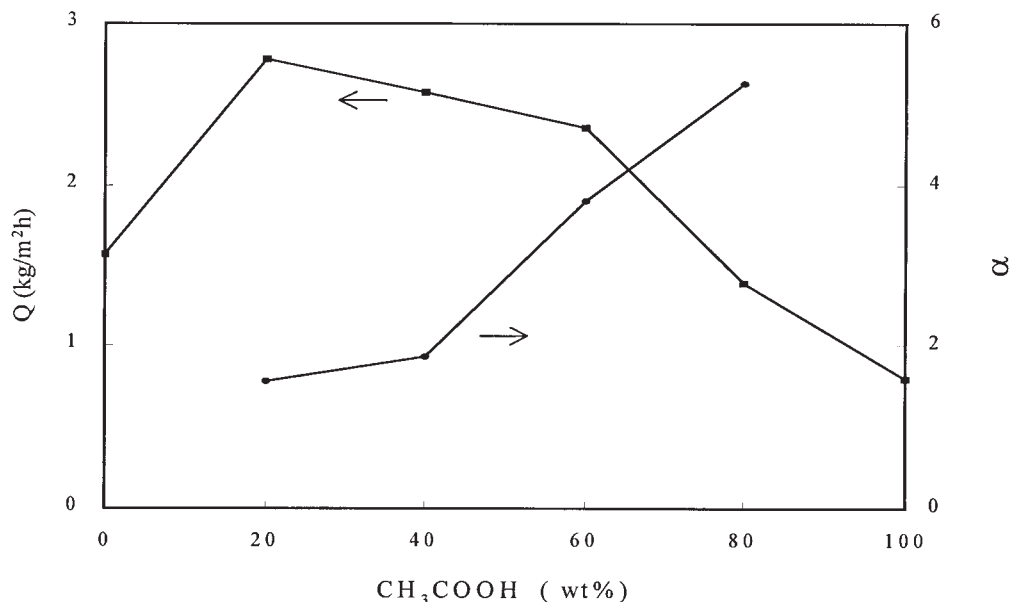
Figure 4 The change of permeation rate and separation factor with the feed composition by using PV method. (■) Q and (●) α.

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 earlier.

From the swelling studies, it was also determined that SD for PVA and PVA-g-4VP membranes were found to be 35 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.[19] They have prepared 4-vinylpyridine-*homografted*-polycarbonate (PC-g-4VP) copolymer membrane in the separation of ethanol–water mixtures by using PV, and concluded that as the percentages of 4VP increases in the copolymer, the SD values of the membranes increase because of the high hydrophilic character of 4VP groups.
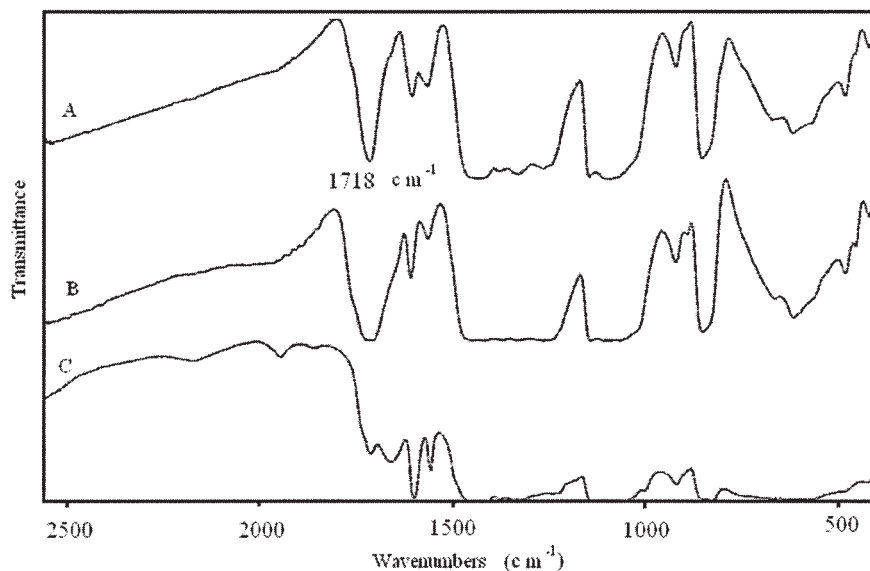

Figure 5 FTIR spectrum of PVA-g-4VP membranes corresponding to the complex formation of pyridine and acetic acid. (a) PVA-g-4VP membranes dipped into CH_3COOH (80 wt %), (b) PVA-g-4VP membranes dipped into CH_3COOH (60 wt %), and (c) PVA-g-4VP.
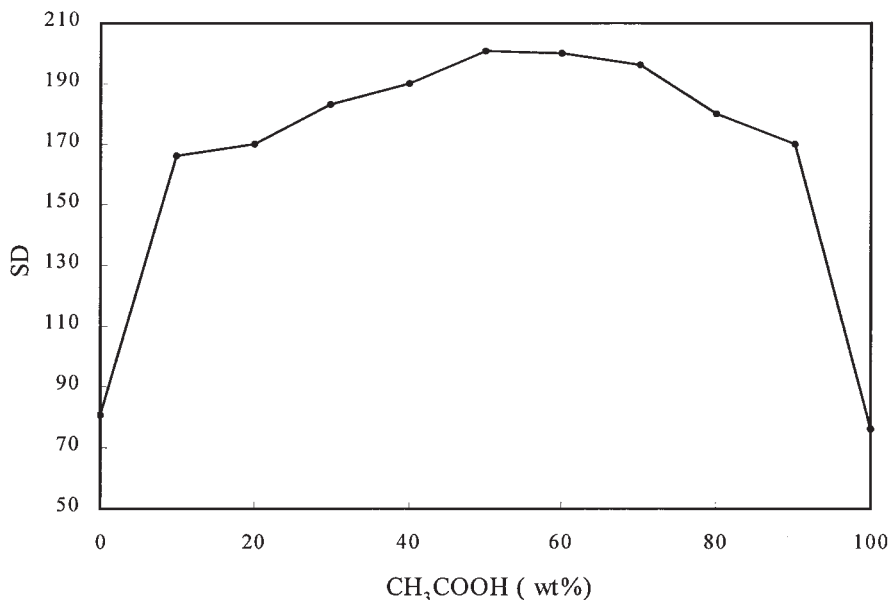
Figure 6 The change of SD with the feed composition for PVA-g-4VP membranes.

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 PV 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.[47] When the system exhibits an ideal permeation behavior, the permeation rate ratio should be equal to unity. When $\theta > 1$, the interactions between polymer and permeants give a positive effect on permeation and
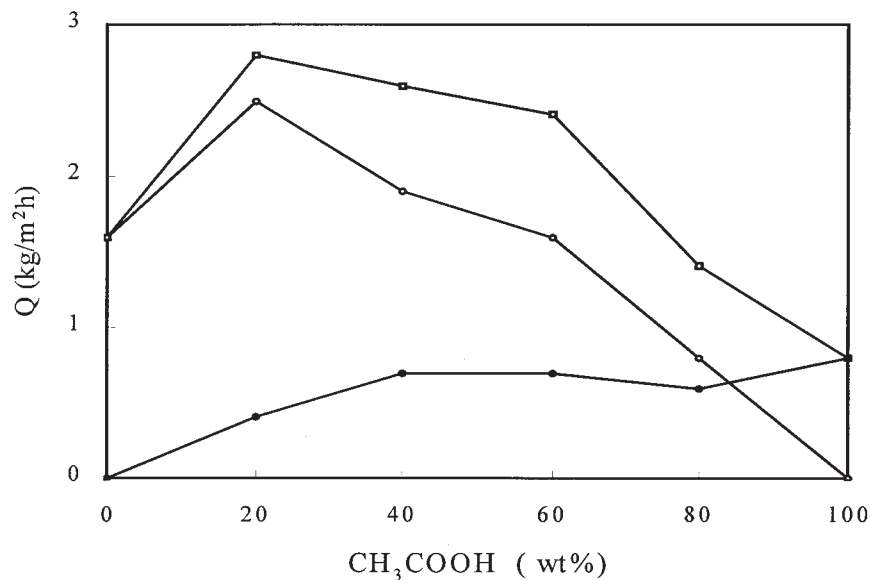

Figure 7 Comparison of the permeation rates of acetic acid and water with the total permeation rate. (□) Q (total), (●) Q (CH$_3$COOH), and (○) Q (H$_2$O).
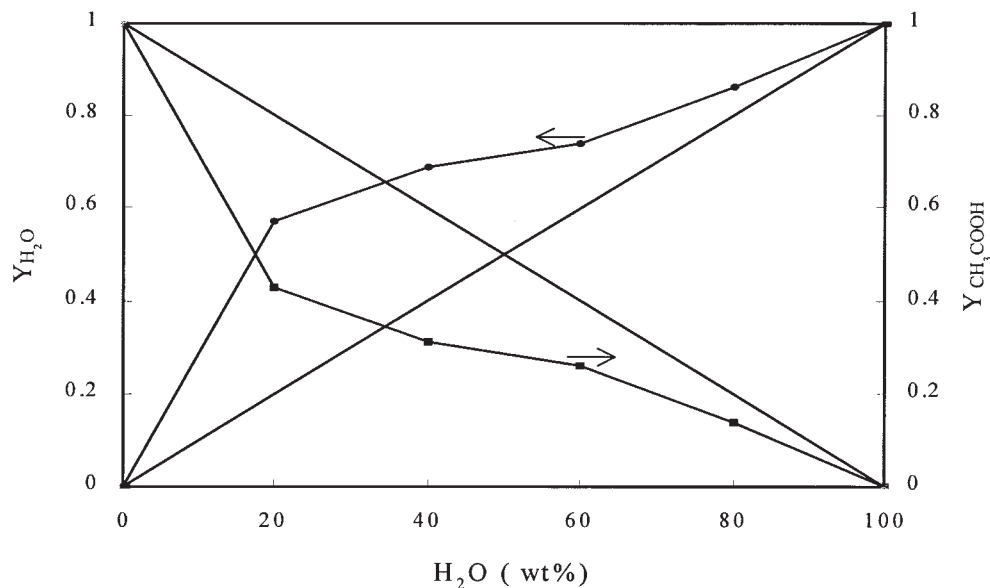
Figure 8 McCabe diagrams of acetic acid and water in the pervaporate for PV. (●) Y (H_2O) and (■) Y (CH_3COOH).

when $\theta < 1$, the interactions effect the permeation negatively.[27,28] The permeation ratios of the acetic acid–water system was calculated by using eqs. (9) and (10) and the results were presented in Figure 9. As it is seen from the figure, θ values of the feed solution and the components are all grater than unity, which means that the presence of one component had affected the permeation behavior of the other positively.

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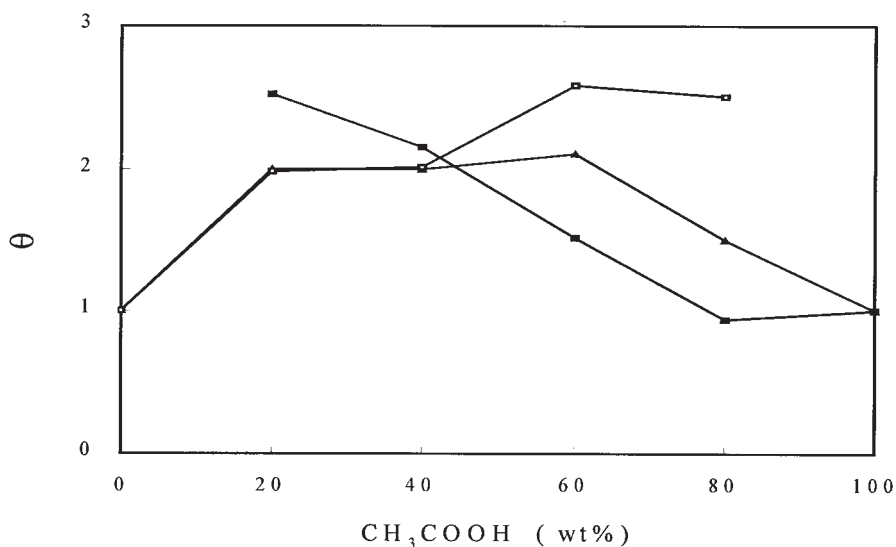

Figure 9 Change of permeation ratios with the composition of the feed mixture. (■) Acetic acid, (□) water, and (△) feed solution.
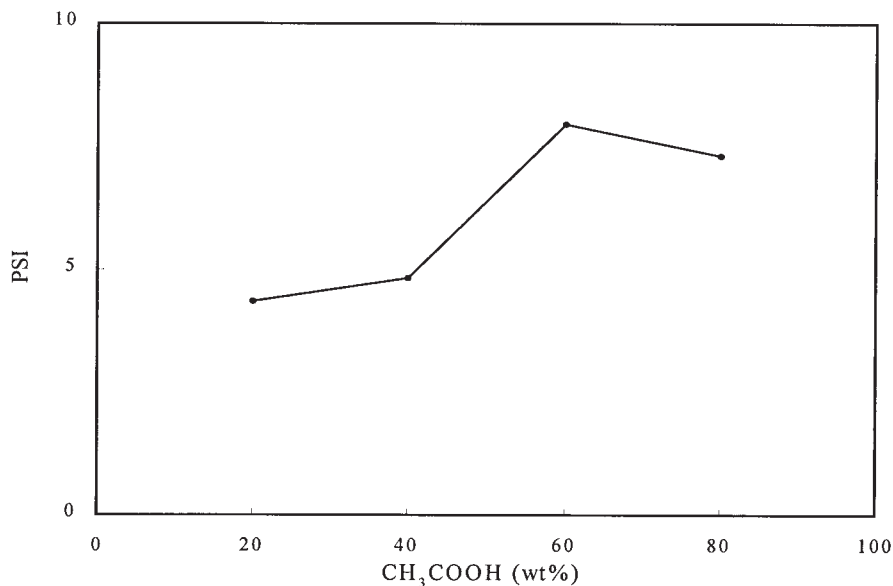
Figure 10 PSI values for PVA-*g*-4VP membranes.

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 PV. 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 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 and so the permeation rate decreases. Additionally, when the acetic acid and water that had been vaporized from the feed mixture come close to the surrounding membrane, acetic acid vapor aggregates much easier than the water vapor because the freezing point of acetic acid is greater than that of water (16 and 0°C respectively). This aggregation of acetic acid molecules is responsible for the permselectivity for water through PVA-*g*-4VP membranes. The compound that is present in the vapor phase in a greater amount with a greater vapor pressure at 40°C (the vapor pressures of water and acetic acid are 55.3 and 34.4 mmHg, respectively, at 40°C) will dissolve in the membrane material, which has lower temperature than the feed mixture, according to Henry's law,
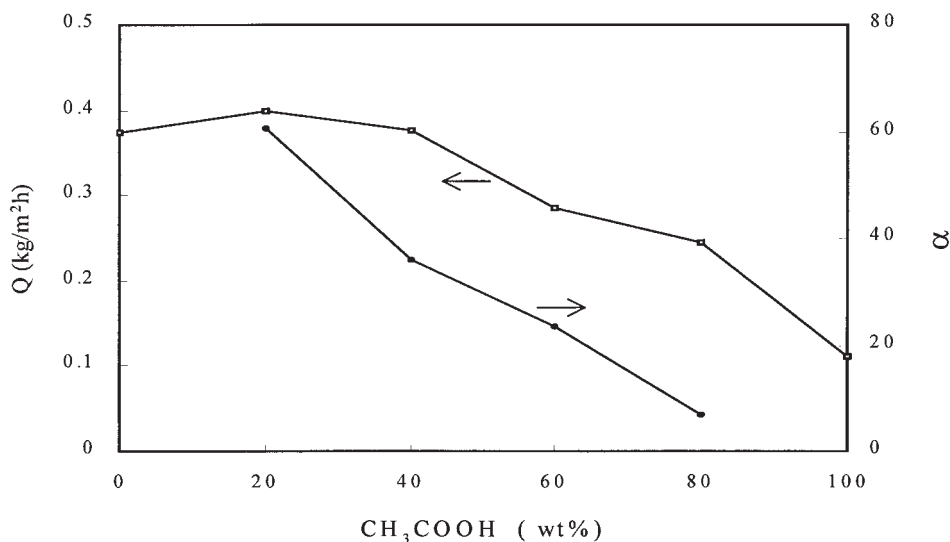

Figure 11 The variation of permeation rates and separation factors of PVA-*g*-4VP membranes with the feed composition by using TDEV method. (□) *Q* and (●) *α*.
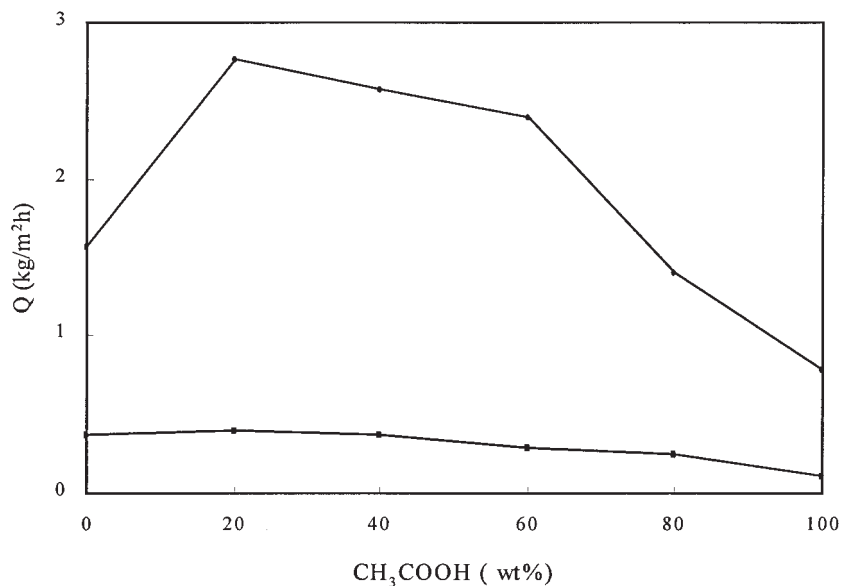
Figure 12 Comparison of permeation rates of PVA-*g*-4VP membranes. (●) PV and (■) TDEV.

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.

Uragami[18] 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, the permeation rates were high in PV method, whereas separation factors were high in TDEV method.

Separation of acetic acid–water azetropic mixtures by using TDEV method

Acetic acid forms an azeotropic mixture with water at a concentration of 3 wt % of CH_3COOH (T_b = 76.6°C).[53] It was separated using PVA-*g*-4VP membranes by TDEV method: the temperature of the membrane surroundings was kept at 40°C, while the feed solution was allowed to be at room temperature. The separation factor and permeation rate were determined as 21 and 0.364 kg/(m^2 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.
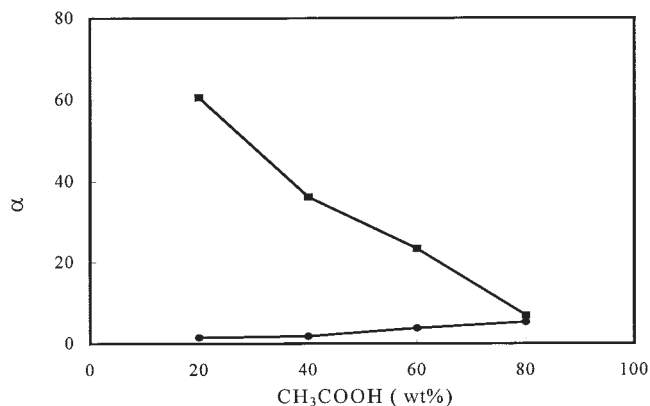

Figure 13 Comparison of the separation factors of PVA-*g*-4VP membranes in PV and TDEV methods. (●) PV and (■) TDEV.

CONCLUSIONS

In the present study, 4VP was grafted on PVA, the membranes were prepared from the grafted copolymer, and then the prepared membranes were used in 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^2 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, whereas the permeation rates (0.10–0.40 kg/(m^2 h)) were 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 kg/(m^2 h).

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