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Characteristics of Permeation and Separation for Acetic Acid–Water Mixtures Through Poly(Vinyl Alcohol) Membranes Modified with Poly(Acrylic Acid)

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ABSTRACT

The pervaporation separation of acetic acid–water mixtures was carried out over the full range of compositions at temperatures varying from 30° to 55°C using poly(vinyl alcohol) (PVA) membranes modified with poly(acrylic acid) (PAA). The best condition for the preparation of the membranes was found as PVA/PAA ratio as 75/25 (v/v). Effects of membrane thickness, operation temperature, feed composition on the permeation flux, and separation factor were investigated. PVA/PAA membranes gave separation factors of 34 to 3548 permeation rates of 0.03 to 0.60 kg/m^2 h, depending on the operation temperature and feed mixture composition. The temperature dependence of permeation rate for binary mixtures was expressed by the Arrhenius type relation and activation energy of 17.62 kcal/mol was calculated for the permeation.

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Key Words: Pervaporation; Separation; Poly(vinyl alcohol) membranes; Modified membrane; Acetic acid–water separation.

INTRODUCTION

Pervaporation separation has emerged as an economical and simple alternative to many separation applications. It is an attractive separation technique for the close boiling point, heat sensitive, azeotropic, and isomeric mixtures and for the removal of organic contaminants from waste water.

Pervaporation (PV) differs from other separation processes in that the membrane constituents a barrier between a liquid in the liquid phase and the permeate in the vapor phase. The separation mechanism in PV is not based on the relative volatility of components, but on the difference in sorption and diffusion properties of the feed substances as well as permselectivity of the membrane.

In recent years, there is increased interest in the use of pervaporation separation processes for the separation of organic liquid mixtures. Most of the research effort on this subject concentrated on the separation of alcohol water system[1–20] but the separation of acetic acid–water mixtures received relatively little attention.[21–29] Acetic acid is one of the top 20 organic intermediates in the chemical industry and because of the small differences in the volatility of water and acetic acid in dilute solutions, azeotropic distillation, an energy intensive process, is required instead of binary distillation. So the pervaporation separation can be an alternative process for saving energy. In the separation of acetic acid–water mixtures poly(acrylic acid)-nylon-6,[21] 4-vinyl pyridine-co-acrylonitrile,[25] chitosan, poly(vinyl chloride), poly(dimethyl siloxane),[30] polycrystalline silicate,[24] acrylonitrile, nafion, and polyimide[22] membranes were used. Using these membranes, relatively low separation factors and permeation rates were obtained.

To get acceptable flux with high selectivity, hydrophilic membranes are required for the separation. PVA is a suitable polymer for the dehydration process because of its good chemical stability, film forming ability, and high hydrophilicity. A drawback is its poor stability in water. To overcome this problem, PVA must be insolubilized by blending,[27] copolymerization,[31] grafting,[21,32] and crosslinking.[11,23,33–35]

Kim, et al.[11] prepared asymmetric PVA membranes by a phase inversion method and crosslinked with gluteraldehyde. They examined the effect of the degree of crosslinking on the pervaporation characteristics.

Yeom and Lee[33] crosslinked PVA membranes with gluteraldehyde by a solution technique and used, in the separation of acetic acid–water mixtures, a range of 70 to 90 wt% in the feed, at temperatures varying from 35° to 50°C.

The enhancement of selectivity of PVA membranes toward water by the introduction of carboxylic acids, such as maleic, amic acid, was also reported.

Huang and Rhim[23] modified PVA using maleic acid, characterized the resulting membranes, and studied the separation of an acetic acid–water system for the entire range of mixture composition at 25°C. The highest separation factor, 7.80, was obtained for 70 wt% acetic acid in the feed.

The characterization of the crosslinking reaction between PVA and amic acid was discussed by Huang and Yeom.[34] They carried out separation of an acetic acid–water mixture over the full range of compositions at temperatures varying from 30° to 70°C.

Poly(acrylic acid) was also used for the modification of PVA membranes. Nguyen et al.[27] concluded that a PVA-poly(hydroxycarboxylic acid) 1:1 blended membrane with a selectivity of 7.9 and permeation rate of $0.06\,\mathrm{kg/m^2\,h}$ respectively, was the most suitable membrane for the dehydration of acetic acid–water mixtures. Rhim et al.[35] characterized the crosslinking reactions between PVA and PAA under various conditions of reaction temperature, reaction time, and the amounts of PAA content.

As it is seen from the cited research results, the selectivity and permeation rates for the separation of acetic acid–water mixtures are still very low. As a part of the studies on the pervaporation separation of acetic acid–water mixtures, PVA was crosslinked by a heat treatment using low-molecular weight PAA through the reaction between the hydroxyl group in PVA and the carboxylic group in PAA and aimed to reach high separation factors with reasonable flux by changing PVA/PAA ratio and the operating conditions, such as membrane thickness, temperature, and feed concentration.

EXPERIMENTAL

Materials

PVA was provided by Merck Chemicals Ltd., UK, with a molecular weight of 72,000. PAA was purchased from Sigma and Aldrich Co., Germany, with an average molecular weight of 2000. Acetic acid was a Merck product.

Preparation of Membranes

Membranes were prepared by using homogenous mixtures of aqueous solutions of PVA and PAA at a concentration of 5.0 wt%. Predetermined amounts of PVA and PAA solution were mixed at room temperature. After being stirred for 1 day, the polymer solution was cast onto petri dishes (4.5 cm in diameter) and allowed to dry at 35°C in an oven. Then, the membranes were removed and heat treated at 150°C for 1 hour. The resulting membranes were preserved in distilled water until use.

Apparatus and Measurements

The apparatus used in pervaporation experiments is illustrated in Fig. 1.

In pervaporation experiments, the permeation cell 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 the cell. The effective area of the membrane was 12.5 cm^2. Feed liquid was poured into the upstream side of the cell and the downstream side was vacuumed. Pervaporation 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 the permeate was analyzed by using Atago Differential Refractometer DD-5 (Atago Co., Ltd., Japan).

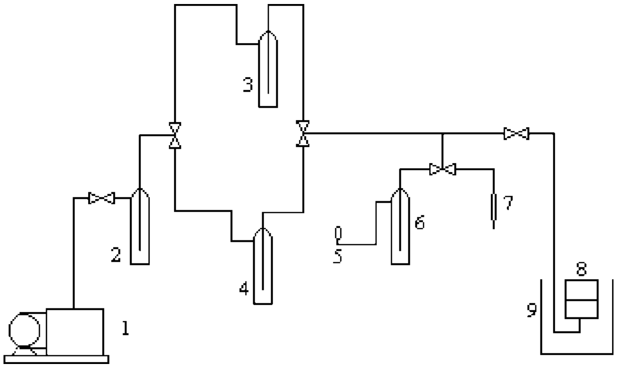

Figure 1. Schematic diagram of the pervaporation apparatus. 1. vacuum pump, 2–4,6. permeation traps, 5. McLeod manometer, 7. vent, 8. permeation cell, and 9. constant temperature water bath.

Performance of the membranes were characterized by separation factor (selectivity) (α), permeation rate (flux) (J), and pervaporation separation index (PSI). The selectivity is given by

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

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.

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

$$J = \frac{Q}{A \cdot t} \qquad (2)$$

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

The pervaporation separation index is calculated using the equation

$$PSI = J \cdot \alpha \qquad (3)$$

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

Swelling Characteristics

The sorption capacity of the membranes was measured by immersing the membrane samples into the acetic acid–water mixtures in the concentration range of 20 to 100 wt% at room temperature. After wiping with the cleansing tissue, the membranes were weighed as quickly as possible. Then, the samples were dried in a vacuum oven at room temperature, until constant weight was obtained. The degree of swelling, DS, was calculated for each membrane as follows:

$$DS = \frac{m_w - m_d}{m_d} \times 100 \qquad (4)$$

where m_w is the mass of swollen sample and m_d is the original mass.

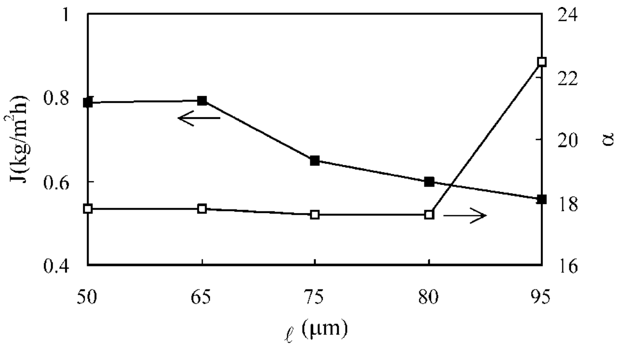

Figure 2. Effect of membrane thickness on permeation rate (■) and separation factor (□). Pervaporation conditions: 20 wt% CH_3COOH, 45°C.

RESULT AND DISCUSSION

Effect of Membrane Thickness

The selectivity and flux as a function of membrane thickness was studied for the separation 20 wt% acetic acid solution at 45°C. Permeation rate and selectivity as a function of membrane thickness (ℓ) is presented in Fig. 2.

As is reflected in the figure, total flux decreases steadily with a membrane thickness higher than 65 μm, whereas, selectivity stays almost constant below a membrane thickness of 80 μm and increases sharply after that.

Figure 3 shows a linear relationship between the total flux and the reciprocal of the membrane thickness as is predicted by the solution-diffusion

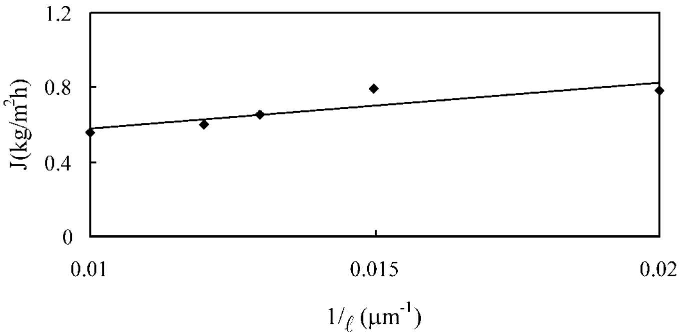

Figure 3. Permeation rate as a function of the reciprocal of the membrane thickness.

model (Fickian behavior). By splitting up the total flux into the component fluxes of water and acetic acid (Table 1). It is clear that total flux is completely controlled by the water flux and that the increase in the thickness had affected the permeation rate of acetic acid more than water.

The influence of membrane thickness on the flux and selectivity was only studied by a few researchers. Different results concerning the effect of membrane thickness on pervaporation performance are reported.[36,37]

Brun et al.[36] studied the influence of membrane thickness on the selectivity using nitrile-rubber membranes for a 60/40 (v/v) mixture of butadiene and isobutane. They concluded that selectivity was constant above a membrane thickness of 100 μm.

Binning et al.[37] concluded that the flux of a mixture of *n*-heptane and isooctane 50/50 (v/v) through a plastic film was proportional to the reciprocal membrane thickness and selectivity was, indeed, independent of the thickness for the membrane, in the range of 20 to 50 μm.

Koops et al.[38] investigated the pervaporation selectivity as a function of membrane thickness for polysulfone, poly(vinyl chloride), and polyacrylonitrile membranes in the dehydration of acetic acid and reported that selectivity decreases with decreasing membrane thickness, below a limiting value of about 15 μm.

Effect of PVA/PAA Ratio on the Separation Factor and the Permeation Rate

Membranes prepared at various volume ratios of PVA and PAA were placed in a pervaporation cell and allowed to permeate at a constant

Table 1. Variation of permeation rates of acetic acid and water with membrane thickness permeation conditions: 20 wt% CH_3COOH, 45°C.

Thickness of membranes (ℓ) (μm)	$J_{Aceticacid}$ (kg/m^2 h) ($\times 10^2$)	J_{Water} (kg/m^2 h) ($\times 10^2$)
50	1.09	77.50
65	1.10	77.90
75	0.90	63.90
80	0.84	58.94
95	0.67	55.10

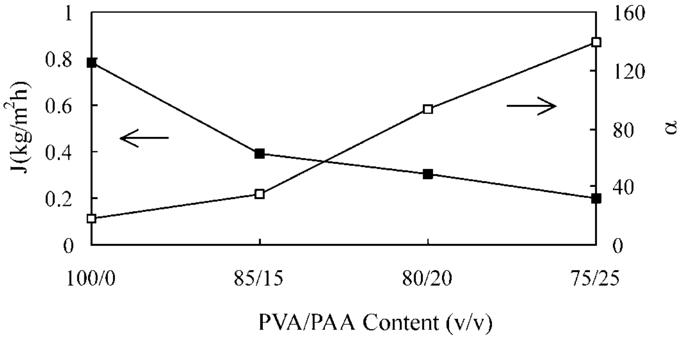

Figure 4. Effect of PVA/PAA content on the permeation rate (■) and separation factor (□). Permeation conditions: 20 wt% CH_3COOH, 45°C.

temperature (45°C), pressure (1.5 mbar), and feed composition (20 wt%). The results are shown in Fig. 4. As is reflected from the figure, permeation rate decreases, whereas, separation factor increases with increasing PAA content in the membrane. Increase in the PAA content increases the crosslinking density in the membrane, as reflected from the swelling degrees given in Table 2. The resulting membrane has a more compact polymeric network structure leading to less free volume in the membrane. This leads to less solubility and diffusivity of the permeating molecules.[33,39,40] Because the molecular size of acetic acid is larger (0.4 nm) than that of water (0.28 nm), the more compact network hinders the transport of the larger component in the feed (Table 3). Therefore the separation factor increases. Similar results were obtained in many other studies..[1,4,27,30,32,41]

Lee et al.[4] used PVA/PAA membranes to separate ethanol–water mixtures by pervaporation. They concluded that as the amount of PAA in the membrane increased, permselectivity toward water increased.

Table 2. Variation of DS of the PVA/PAA membranes in 20 wt% CH_3COOH.

PVA/PAA (v/v)	DS
100/00	40
85/15	45
80/20	33
75/25	18

Table 3. Variation of the permeation rates of acetic acid and water with PAA content permeation conditions: 20 wt% CH_3COOH, 45°C, 50 μm.

PVA/PAA (v/v)	$J_{Aceticacid}$ (kg/m^2 h)(× 10^2)	J_{Water} (kg/m^2 h)(× 10^2)
100/00	1.09	77.50
85/15	0.27	38.92
80/20	0.08	30.12
75/25	0.04	19.96

Nguyen et al.[32] reported that a polyacid component favored the transport of water over that of acetic acid by preferential interactions in the pervaporation of acrylic-acid grafted membranes.

In the present study PVA/PAA ratio was taken as 75/25 (v/v). Because membranes become so brittle that they cannot be separated from glass petri dishes at PAA contents higher than this. Membranes containing PAA at this ratio were found to be suitable from mechanical point of view in the separation of acetic acid–water mixtures.

Effects of Operation Temperature on the Separation Performance

The effect of temperature on the separation performance of PVA/PAA membranes is shown in Fig. 5. The permeation rate increased, whereas, the separation factor decreased when the pervaporation experiments were carried out in the 30° to 55°C temperature range.

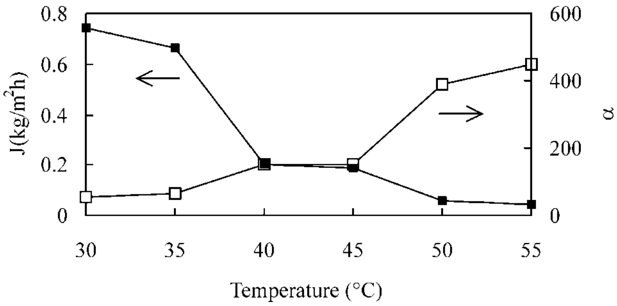

Figure 5. Change of permeation rate (■) and separation factor (□) with operation temperature. Permeation conditions: 20 wt% CH_3COOH, PVA/PAA:75/25.

The general trend in the effect of temperature on the flux and separation factor can be explained by free-volume theory.[34] According to the theory, the thermal motion of polymer chains in the amorphous regions randomly produces free volume. As temperature increases, the frequency and amplitude of the chain jumping (i.e., thermal agitation) increase, and the resulting free volumes become larger. In pervaporation, the permeating molecules can diffuse through these free volumes. Thus, when the temperature is high, the diffusion rates of both of the isolated permeating molecules and associated permeating molecules are high, so that the total permeation rate could be high and separation factor low. This phenomenon can also be explained in terms of the plasticizing effects of the permeants and the interactions between permeants and the polymer. Strong interactions can be formed at low temperature and reduce the plasticizing effect. However, as the temperature increases, interaction becomes weaker, so that the plasticizing effect can be recovered.

Similar results were observed in the separation of acetic acid mixtures using amic acid crosslinked PVA membranes[42] and in the alcohol–water separation using poly(acrylic acid) membranes. [12]

The permeability of pervaporation membranes decrease linearly with reciprocal of temperature following an Arrhenius type relation of the form.[12,32,34,42,43]

$$J = A_p \cdot e^{-Ep/RT}$$

where A_p and E_p are the preexponential factor and overall activation energy for permeation, respectively. Figure 6 shows that the permeation rate is inversely proportional to the absolute temperature, indicating that

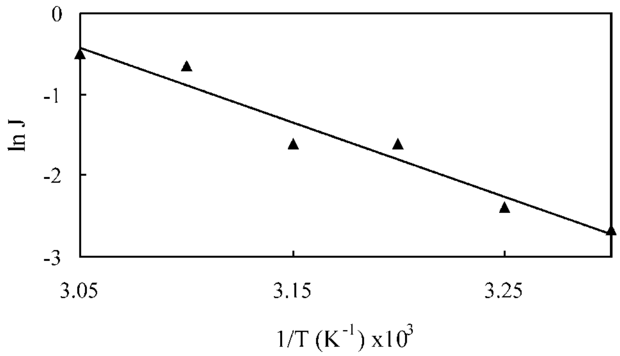

Figure 6. Arrhenius plot of lnJ vs. 1/T for PVA/PAA membranes.

experimental results agree well with Arrhenius equation. The activation energies of acetic acid–water permeating through the PVA/PAA membrane were calculated to be 17.62 kcal/mol.

On the whole, although the separation factor of 550 is obtained at 30°C, flux was very low. For this reason, 40°C was selected as the best operating temperature in the rest of the study, with a reasonable flux 0.20 kg/m^2 h and separation factor 152.

Effect of Feed Composition on Pervaporation

The pervaporation separation of acetic acid–water was carried out over a range of 20 to 80 wt% acetic acid in the feed. The results are shown in Fig. 7.

Separation factor and total flux were 150 to 3548 and 0.03 to 0.20 kg/m^2 h respectively, depending on feed composition. Total flux decreased rapidly, first with the addition of acetic acid to water, and then slowed down with further increases in acid concentration. The separation factor increased monotonously as the acetic acid content of the feed increased. Details on this can be obtained through the examination of the degree of swelling curve presented in Fig. 8. As reflected from Fig. 8, swelling of PVA/PAA membrane decreases up to 10% by weight acetic acid content in the feed solution due to the decrease in the plasticizing action of water with the addition of acetic acid. It then increases up to 40 to 50 wt% acetic acid content.

Reduction in swelling degree is observed with the further increase in acetic acid concentration. An increase in the swelling curve up to 40 wt% acetic acid content can be attributed to the plasticizing effects of both water

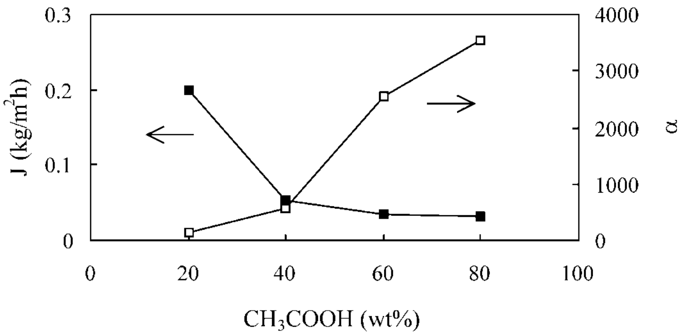

Figure 7. Variation of permeation rate (■) and separation factor (□) with feed composition. Permeation conditions: PVA/PAA:75/25, 40°C.

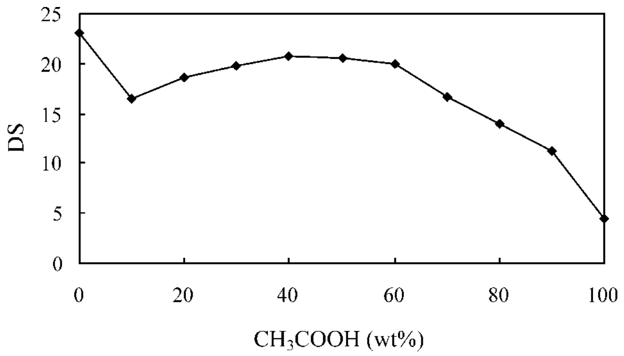

Figure 8. Change of degree of swelling of PVA/PAA:75/25 membranes with varying feed compositions.

and acetic acid on the membrane. However, interaction of permeating molecules decrease the flux (see Fig. 7). The decrease of weight fractions of water in the feed causes a strong hydrogen bonding interaction among carboxyl or carbonyl groups. This strong self-interaction hinders the incorporation of water into the membrane. As a result, the flux decreases with decreasing water concentrations in feed. Decrease in swelling degree over 50% by weight acetic acid content in the feed is probably due to the decrease in water content of the feed since the plasticizing action of acetic acid is less than that of water.

For comparison purposes, some results regarding the separation of acetic acid–water mixtures obtained by various researchers with different types of membranes are listed in Table 4. One can see that PVA/PAA membrane has high-permeation rate and selectivity, depending on the feed composition and temperature, than the membranes studied up to now.

Pervaporation separation index values were calculated[34,42] and are presented in Fig. 9. As is reflected from the figure, performance of the PVA/PAA membranes are good, especially at high acetic acid concentrations, from the selectivity point of view.

Separation of Acetic Acid–Water Azeotropic Mixtures

Acetic acid–water azeotropic mixture (3 wt% CH$_3$COOH, $T_b = 76.6°C$),[44] was separated with 75/25 (v/v) PVA/PAA membranes at

Table 4. Comparison of the performance of the membranes based on PVA for the pervaporation separation of acetic acid-water mixtures.

Polymer	Nature of the membrane preparation method	Feed (%) composition (m/m)	Temperature (°C)	Permeation rate (J) (kg/m^2 h)	Separation factor (α)	Reference
PVA	Crosslinking with gluteraldehyde	70–90	35–50	0.03–0.26	120–420	[33]
PVA	Crosslinking with amic acid	0–100	30–70	0.08–2.28	13–42	[34]
PVA	Crosslinking with maleic acid	70	25	0.20–2.80	4.0–7.8	[23]
PVA/ PHCA	Blending with poly(hydroxy carboxylic acid) (PHCA)	0–90	25	0.06–0.35	4.0–7.9	[27]
PVA	Carboxymethylated PVA	65–98	40	0.10–0.55	6.0–7.5	[32]
AA-g-PVA	Acrylic acid (AA) grafted PVA	0–40	20–60	0.20–0.90	1.5–6.6	[32]
PVA/PAA	Modification with poly(acrylic acid) (PAA)	0–80	30–55	0.03–0.60	34–3548	This study

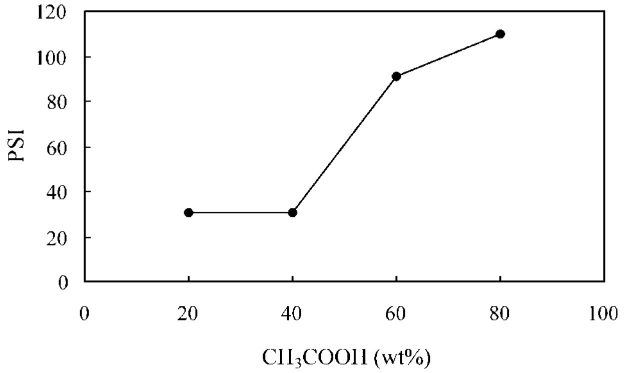

Figure 9. Effect of feed composition on the permeation separation index of PVA/PAA membranes.

40°C using pervaporation technique; the separation factor and permeation rate were determined as 291 and 0.20 kg/m^2 h, respectively.

CONCLUSION

From studies on the pervaporation separation of acetic acid–water mixtures, the following conclusions may be drawn.

Selectivity of PVA membranes in the pervaporation of acetic acid–water mixture is enhanced by modifying with a PAA. Membranes prepared at PVA/PAA:75/25 (v/v) solution content in the reaction solution had the best separation performance.

With the increase in temperature, the permeation rate increased, whereas, the separation factor decreased when the experiments were carried out at 30 to 55°C temperature range. A temperature of 40°C was selected as optimum operating temperature.

Flux decreased, whereas, the selectivity increased as the acetic acid content of the feed increased. Membranes showed good separation performance, especially at high acetic acid concentrations.

Azeotropic acetic acid–water mixture was separated with a separation factor of 291 and a flux of 0.20 at 40°C.

The PVA/PAA:75/25 membranes yielded good separation performance with a separation factor of 3548 and flux of 0.03 kg/m^2 h at 40°C using 50 μm membranes.

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