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Permeation and Separation Characteristics of Acetic Acid-Water Mixtures by Pervaporation through Acrylonitrile and Hydroxy Ethyl Methacrylate Grafted Poly(vinyl alcohol) Membrane

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Abstract: In this study, acrylonitrile (AN) and hydroxyl ethyl methacrylate (HEMA) were grafted onto poly(vinyl alcohol) (PVA) using cerium (IV) ammonium nitrate as initiator at 30°C. The graft copolymer was characterized using the Fourier transform infrared spectroscopy (FTIR) and elemental analysis. The grafted PVA membranes (PVA-g-AN/HEMA) were prepared by a casting method, and used in the separation of acetic acid-water mixtures by pervaporation. The effects of the membrane thickness, operating temperature, and feed composition on the permeation rate and separation factor for acetic acid-water mixtures were studied. Depending on the membrane thickness, the temperature and feed composition PVA-g-AN/HEMA membranes gave separation factors 2.26–14.60 and permeation rates of 0.18–2.07 kg/m^{2}h. It was also determined that grafted membranes gave lower permeation rates and greater separation factors than PVA membranes. Diffusion coefficients of acetic acid-water mixtures were

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calculated from permeation rate values. The Arrhenius activation parameters were calculated for the 20 wt.% acetic acid content in the feed using the permeation rate and the diffusion data obtained at between 25–50°C.

Keywords: Graft copolymer, PVA membranes, pervaporation, acetic acid-water mixtures, separation

INTRODUCTION

Pervaporation has been recognized as a promising separation process because of its effective and economical separation of liquid mixtures, especially water-organic mixtures with an azeotrop and/or small differences in boiling characteristics (1–3). Acetic acid is one of the top 20 organic intermediates used in the chemical industry and its mixtures with water is encountered in the preparation of several intermediates like acetic acid itself, vinyl acetate, acetic anhydride, phthalic anhydride, etc. The separation of acetic acid from water by normal binary distillation is difficult due to low relative volatility, especially at high acetic acid concentrations and thus more energy intensive and expensive azeotropic distillation or sometimes solvent extraction is used (4).

For this reason, the pervaporation membrane separation process can be one of the alternate process candidates for saving energy. This process offers an effective recovery from aqueous media and avoids the limitation of osmotic pressure imposed on reverse osmosis processes by maintaining the permeate below its saturated vapor pressure. Although vaporization of a part of the liquid charge is required in this process, the permeation pressure can be reduced by vacuum pumping or gas sweeping. In general however, pervaporation can be of practical use only when the selectivity of the transfer is much higher than for an ordinary vaporization and when the rate of permeation is satisfactorily large.

In recent years the research emphasis has been on the development of new polymer membranes (5–14), which have high separation factors and acceptable permeation rates with good stability in the acetic acid-water mixtures to be separated.

Several permselective membranes for water have been tried from hydrophilic polymers such as poly(acrylic acid)-nylon 6 (5), poly(acrylic-co-styrene) (15), poly(4-vinylpyridine-co-acrylonitrile) (11), nafion (4, 8), PVA blended with poly(vinyl pyrolidone) (16), and sodium alginate blended guar gum-g-polyacrylamide (17), for this purpose, but very few of these are effective for the dehydration of acetic acid.

PVA is a possible candidate for the separation of acetic acid-water mixtures due to its properties as low cost, chemical stability, film-forming ability, and high hydrophilicity. However it has a drawback of poor stability in water. Thus it must be insolubilized by modification reactions as blending (16), grafting (5, 18), or crosslinking (6, 9, 12, 14) to form a stable membrane with good mechanical properties and selective permeability to water.

In our previous work (19), acrylonitrile grafted PVA (PVA-g-AN) membranes at different combinations were prepared and used in the separation of acetic acid-water mixtures by pervaporation. In the present study, we have aimed to improve pervaporation separation and permeation characteristics of PVA-g-AN membrane with HEMA. For this reason, AN and HEMA together were grafted onto PVA using cerium (IV) ammonium nitrate, at 30°C. Prepared membranes from the graft copolymer were used in the separation of acetic acid-water mixtures by pervaporation. The effects of the membrane thickness, the operating temperature, and the feed concentration on the pervaporation performance of the membranes have been investigated and discussed.

EXPERIMENTAL

Materials

PVA was purchased from Merck (Darmstadt, Germany). The molecular weight and the degree of saponification were 72,000 and $>$% 98, respectively. AN and HEMA were supplied by Merck and purified by reduced pressure distillation. Cerium (IV) ammonium nitrate (CeAN) (Merck) was used after vacuum drying. Acetic acid (extrapure grade), dimethylformamide (DMF), dimethylsulfoxyde (DMSO), and nitric acid were products from Merck and were used as received. Other reagents used in the study were also all Merck products.

Synthesis of Graft Copolymer

The graft copolymerization of AN and HEMA onto PVA was carried out in water using cerium (IV) ammonium nitrate/nitric acid as an initiator at 30°C for 3 hours in N_2 atmosphere. 5 gram of PVA was dissolved in 95 mL of distilled water by stirring and heating to 80°C. Various percentages of AN and HEMA were added to the PVA solution. Stirring was continued for 1 h under N_2 atmosphere. At this stage 20 mL of CeAN (1.0×10^{-2} M)/HNO_3 (1.0×10^{-2} M) solution was added to the reaction mixture. After a specified time interval, the reaction was quenched with 10 mL of aqueous ferrous salt solution ($FeSO_4$) (5.0×10^{-2} M) and pH of graft copolymer latexes were adjusted to 1.5 with 1.0 M HCl solution, then dried in air at room temperature. The product was extracted with water at 80°C, then with DMF at 55°C for 2 days to remove the unreacted PVA, polyacrylonitrile (PAN), and poly(hydroxy ethyl methacrylate) (PHEMA) homopolymers. After the extraction, the grafted polymer was vacuum-dried at 60°C for 48 h (20).

Membrane Preparation

1.2% (w/v) solution of PVA-g-AN/HEMA was prepared by dissolving preweighted quantities of dry copolymer in DMSO and heated at 80°C for at least 6 h. The solutions of 20–30 mL were cast onto petri dishes and the solvent was evaporated at 80°C to form the membrane. The dried membranes (30–70 μm) were stored in distilled water for further use.

Heat treated PVA membranes were also prepared by casting method from 7% (w/v) PVA solution (40 μm) for comparison purposes (19).

Infrared Analysis

FTIR spectra of PVA and grafted PVA were taken with Mattson 1000 Fourier Transform Infrared Spectrometer.

Swelling Measurements

The dried membrane samples were immersed in acetic acid-water mixtures of different concentrations at 25°C for at least 48 h. Membranes were weighted as quickly as possible, after being wiped with the cleansing tissue. Then the samples were dried in a vacuum oven at room temperature until constant weight. The swelling degrees, SD, were calculated as follows:

$$SD = \frac{w_s}{w_d} \tag{1}$$

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

Pervaporation

The apparatus used in this study was illustrated in Fig. 1. The pervaporation cell was a two glass compartment cell with a 150 mL upper compartment, 75 mL of lower compartment, which fastened together by joints. Membranes were placed on to the porous glass support in the cell. The effective membrane area was 12.5 cm^2. The pressure at the downstream side was kept at 23 Pa by a vacuum pump (Vacuu Brand RD 15, GMBH Co., Germany). Pervaporation experiments were conducted at constant temperatures ranging from 25–50°C using different feed compositions. Upon reaching steady state flow conditions, the permeate vapor was collected in liquid nitrogen traps and weighed. The composition of the permeates was deducted by measuring the refractive indices with Atago

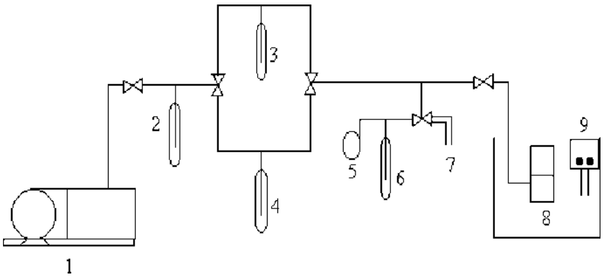

Figure 1. Schematic diagram of pervaporation apparatus used in this study.1. Vacuum pump 2,3. Trap 4,6. Cold traps for collecting samples 5. Vacuum monometer 7. Vent to atmosphere 8. Permeation cell 9. Water bath with temperature indicator.

DD-5 type digital differential refractometer (Atago Co., Ltd., Japan) (accuracy ± 0.001) with the aid of a calibration curve for acetic acid-water mixture prepared using known quantities of the two components. The performance of the membranes was expressed by separation factor (selectivity), permeation rate (flux), and pervaporation separation index. The separation factor, α, is given by

$$\alpha = \frac{Y_{H_2O}/Y_{CH_3COOH}}{X_{H_2O}/X_{CH_3COOH}} \tag{2}$$

where X_{H_2O}, X_{CH_3COOH}, Y_{H_2O} and Y_{CH_3COOH} are the weight fractions of water and acetic acid in the feed and in the permeate respectively. Water is the preferentially permeating component.

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

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

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

The pervaporation separation index (PSI) is calculated by using the following equation (5, 13, 14)

$$PSI = J \cdot \alpha \tag{4}$$

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

RESULTS AND DISCUSSION

IR Spectra Analysis and Elemental Analysis Results

IR spectra of PVA and grafted PVA were shown in Fig. 2. The stretching vibrations of –OH and –CH appears at 3349 cm^{-1} and 2945–2910 cm^{-1},

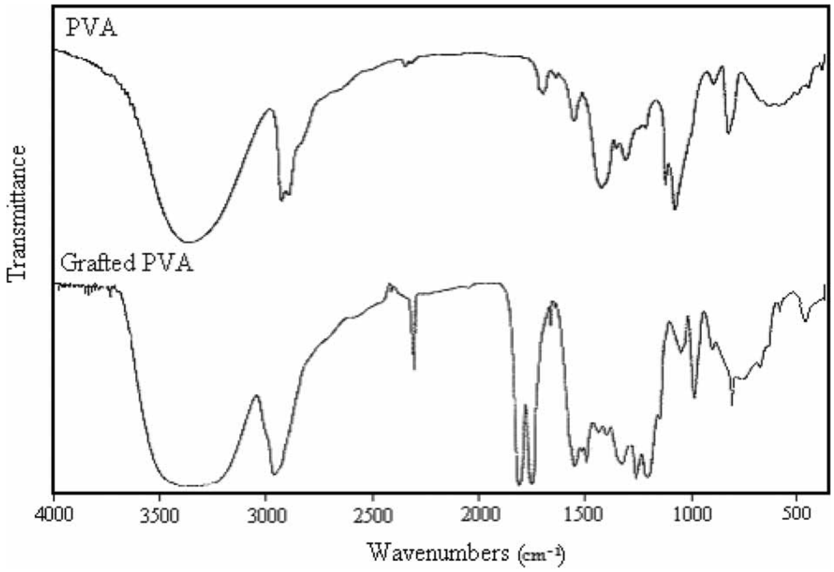

Figure 2. FTIR spectra of PVA and grafted PVA.

respectively. As it is also seen from the figure that the absorptions at 1725 cm^{-1} and 1664 cm^{-1} in the grafted PVA are typical to the ester (—CO—O—) band and vinyl (—C=C—) band of the HEMA respectively (21–23). The strong band appearing at 2237 cm^{-1} in the grafted PVA corresponds to –CN stretching vibrations of acrylonitrile (4). It is clear that the spectral changes are evidences grafting reaction onto PVA.

Composition of the grafted membranes was calculated using following equations (20) from the elemental analysis results and given in Table 1.

$$a = 0.65935H + 9.42 \times 10^{-2}N - 9.15 \times 10^{-2}C \quad (5)$$

$$b = 3.79 \times 10^{-2}N \quad (6)$$

$$c = 10.81 \times 10^{-2}C - 13.92 \times 10^{-2}N - 0.6493H \quad (7)$$

Where a, b, and c display weight percentage of PVA, AN and HEMA, respectively. C, H, and N also display the values of elemental analysis results. As it is seen from the table, HEMA is the dominantly grafted monomer and percentage of nitrogen in the membrane decreased with the increase in HEMA content. The presence of nitrogen in the grafted PVA and the decreasing content of it with the HEMA also confirm the grafting process. PVA-g-AN/HEMA1 membrane was not selected for pervaporation studies due to its low mechanical strength. PVA-g-AN/HEMA3 could not be used since it would break up in acetic acid concentrations higher than 50 wt.%. For these reasons, the PVA-g-AN/HEMA2 membrane was

Table 1. Elemental analysis results of grafted PVA and composition of grafted membrane

Membrane	PVA/AN/HEMA (w/w/w)	C (%)	H (%)	N (%)	Composition of grafted membrane (w/w) (%) PVA	AN	HEMA
PVA-g-AN/HEMA1	1/2.5/1	54.57	7.48	3.53	26.9	13.4	59.7
PVA-g-AN/HEMA2	1/3.5/1	56.09	6.68	9.32	15.0	35.3	49.7
PVA-g-AN/HEMA3	1/3.5/1.5	54.61	7.38	4.25	27.1	16.1	56.8

selected to use in the pervaporation experiments due to its good mechanical strength.

Effect of Membrane Thickness

Membranes with varying thicknesses (30–70 μm, average of at least ten measurements) were prepared from the copolymer by the casting method. The permeation rate and separation factor as a function of membrane thickness were studied for 20 wt.% acetic acid solutions at 30°C and the results are presented in Fig. 3. As it is reflected from the figure that increase in the membrane thickness decreases the permeation rate gradually whereas it increases the separation factor up to a membrane thickness of 50 μm, then stays almost constant till 70 μm.

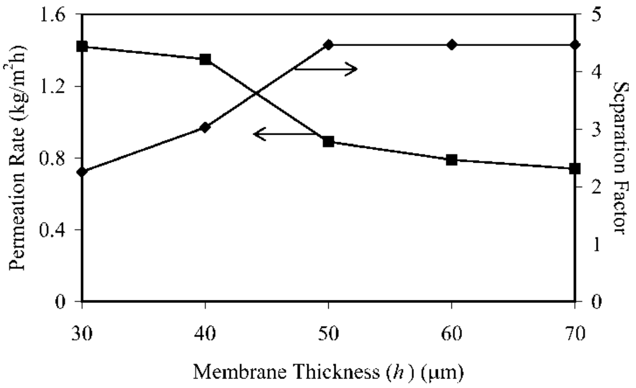

Figure 3. Effect of membrane thickness on the permeation rate (■) and separation factor(◆). Permeation conditions: 20 wt.% CH_3COOH, T = 30°C.

Figure 4 shows an approximately linear relationship between the permeation rate and the reciprocal of the membrane thickness as is predicted in the solution-diffusion model (Fickian behavior).

The total permeation rate was split up to the component permeation rate of water and the acetic acid (Table 2). It is clear that the total permeation rate is completely controlled by the water permeation rate and an increase in the thickness had affected the permeation rate of acetic acid more than water. In our previous studies, similar results were found for the separation of acetic acid-water mixtures using PVA-g-AN (19), malic acid (MA) cross-linked PVA (24) and poly(acrylic acid) (PAA) membranes (25).

Different results concerning the effect of membrane thickness on the pervaporation performance was also reported in the literature (26–28).

Koops et al (26). investigated the pervaporation selectivity as a function of membrane thickness for the polysulfone, poly(vinyl chloride) and poly(acrylonitrile) membranes in the dehydration of acetic acid and reported that selectivity decreases with decreasing membrane thickness below a limiting value of about 15 μm.

Binning et al. (27). reported that the permeation rate of a mixture of n-heptane and isooctane through a plastic film was proportional to the reciprocal of membrane thickness and the separation factor was indeed independent to the thickness for the membranes 20–50 μm thicknesses.

In the present study membranes of 40 μm thickness were preferred in the rest of the study due to their acceptable permeation rate and the separation factor.

Effect of Operating Temperature in Pervaporation

Figure 5 exhibits the effect of the operating temperature on the permeation rate and the separation factor of the grafted PVA membrane for a 20 wt.% acetic

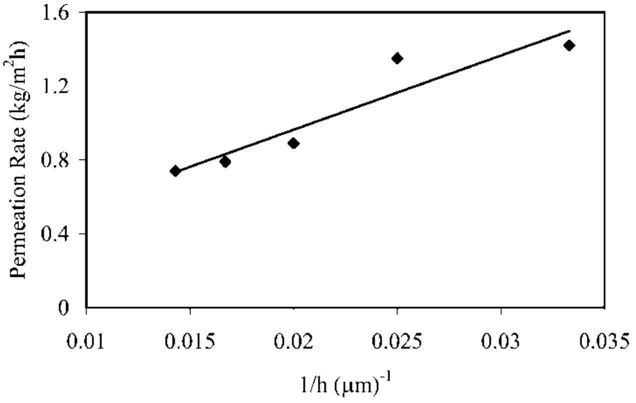

Figure 4. Permeation rate as a function of the reciprocal of the membrane thickness.

Table 2. Variation of permeation rates of water and acetic acid with membrane thickness for 20 wt.% acetic acid at 30°C

Thickness of membranes (μm)	$J_{water} \times 10^1$ (kg/m^{2}h)	$J_{acetic\ acid} \times 10^1$ (kg/m^{2}h)
30	12.79	1.41
40	12.47	1.03
50	8.43	0.47
60	7.48	0.42
70	7.01	0.39

acid solution. As expected, when the temperature was increased the total permeation rate increased, but the separation factor decreased. According to the free volume theory, the thermal motion of polymer chains in the amorphous regions randomly produces free volume (13). As the temperature rises, the frequency and amplitude of chain jumping increase and diffusion rate of individual permeating molecules becomes 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 with increasing the operating temperature. As a result, the permeation rate increases and the separation factor towards water decreases. Similar trends were also reported in the literature by other workers (13, 29–32).

Aminabhavi and Naik (33) prepared grafted copolymeric membranes of PVA with acrylamide (PVA-g-AAm) and used in the pervaporation separation

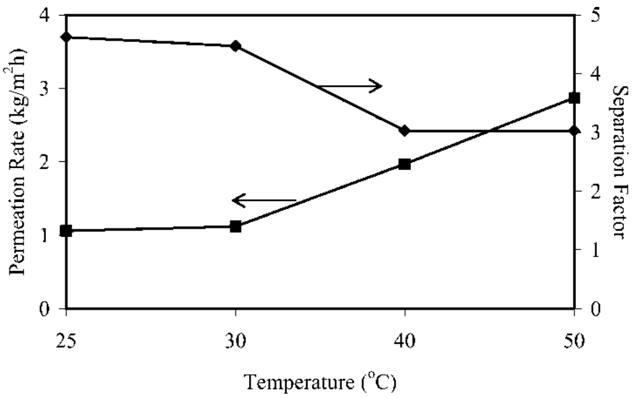

Figure 5. Change of permeation rate (■) and separation factor (◆) with operation temperature. Permeation conditions: 20 wt.% CH_3COOH, h = 40 μm.

of water-dimethylformamide mixtures. They have found that the permeation rate increases with increasing feed temperature, but the separation factor decreases.

Lee et al. (34) investigated the pervaporation separation of binary organic-aqueous liquid mixtures using crosslinked PVA membrane. They observed that permeation rates increase with an increasing operating temperature and decrease with an increasing PAA content in the resulting membrane.

Although the separation factor of 4.62 is obtained at 25°C, the permeation rate was low. For this reason 30°C is selected as operating temperature in the rest of the study with a reasonable permeation rate (1.12 kg/m^{2}h) and separation factor (4.47).

Effect of Feed Composition in Pervaporation

Pervaporation separation of acetic acid-water mixtures was carried out over a range of 10–90 wt.% acetic acid in the feed using PVA-g-AN/HEMA and PVA membranes at 30°C. The results obtained were shown in Fig. 6. In this range of acetic acid concentration the separation factor increases slowly with the acetic acid content up to 70 wt.%, then increases sharply, whereas the permeation rate decreases continuously. As can also be seen from the figure, the separation factors of the grafted membrane were better than that of the PVA membrane whereas the permeation rate of the PVA membrane were higher than the grafted membrane due to the grafting confirmed in Table 1 and Fig. 2.

The PVA is a highly hydrophilic polymer and has poor stability in water. The presence of AN, which is hydrophobic in nature, enhances the strength of the PVA membrane whereas the presence of HEMA, which is hydrophilic in

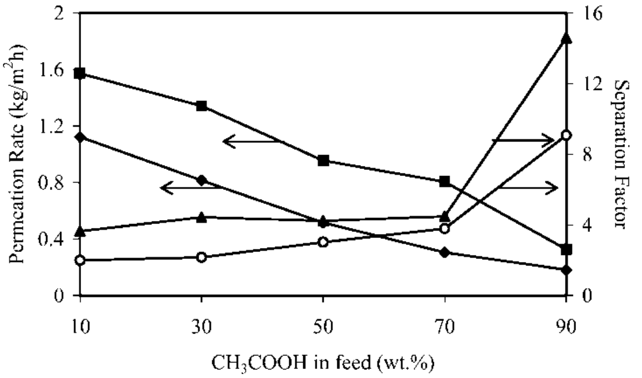

Figure 6. Variation of permeation rate of PVA (■), PVA-g-AN/HEMA (◆) and separation factor of PVA (O), PVA-g-AN/HEMA (▲) with feed composition. Permeation conditions: $h = 40$ μm, T = 30°C.

nature, improves the hydrophilicty of the PVA membrane. So, the PAN-PHEMA component introduced by the grafting reaction made the membrane non-soluble but easily swellable due to occurrence of hydrophilic and hydrophobic balance. An increase in the separation factor of the grafted PVA membrane compared to PVA membrane is caused from a hydrogen bonding interaction between–COOH groups of acetic acid and –CN groups of AN; thus it becomes difficult for acetic acid molecules to diffuse through the membrane and the separation factor toward water increases. In addition, the introduction of AN into PVA made the structure of the membrane dense (20). Thus both the solubility and diffusivity of the permeating liquid through the membrane decline, which depresses the permeation rate but increases the separation factor.

The transport mechanism in pervaporation through polymeric membranes can be described by solution-diffusion model (19, 27). The membrane performance depends upon the sorption of permeants in the feed and their diffusion through the membrane. When the transport of species through the membrane is due to this mechanism, the size of the permeating species is very important in the solution or diffusion processes. The molecular size of water (0.28 nm) is smaller than acetic acid (0.40 nm) (35). In addition, water has a much more hydrophilic character than acetic acid. Therefore, water molecules in pervaporation can be selectively incorporated into the hydrophilic membrane and predominantly diffused. Consequently, the permeation rate decreases while the separation factor increases with the decrease in the water content of the feed.

Looking at the permeation rate of each individual component in Fig. 7, the water permeation rate is too large compared with that of acetic acid, so the shape of the water permeation rate curve is almost similar to that of the total permeation rate. The water permeation rate decreased with the acetic acid content as the total permeation rate did while the acetic acid permeation rate has a maximum value at 50 wt.% acetic acid, that is the permeation enhancement of acetic acid was found up to this concentration. As is also seen from Fig. 8, the swelling of the grafted membrane increases up to 50 wt.% acetic acid content, then decreases sharply. This can be explained in terms of the plasticizing effect of both water and acetic acid on the membrane (13). Up to the acetic acid concentration of 50 % by weight acetic acid, the plasticizing action of the water enhances the acetic acid permeation by decreasing the energy required for diffusive transport of acetic acid through the membrane, resulting in an increase in the separation factor. At high acetic acid concentrations the decrease in the weight fraction of the water in feed causes decrease in the swelling of the membrane (Fig. 8). As a result the permeation rate decreases and the separation factor increases with decreasing water concentration in the feed.

Similar results concerning the effect of feed composition on pervaporation performance was reported in the literature (12, 36).

Yeom and Lee (12). studied the pervaporation separation of water–acetic acid mixtures through poly(vinyl alcohol) membranes crosslinked with glutaraldehyde. They concluded that the permeation rate decreased with the acetic

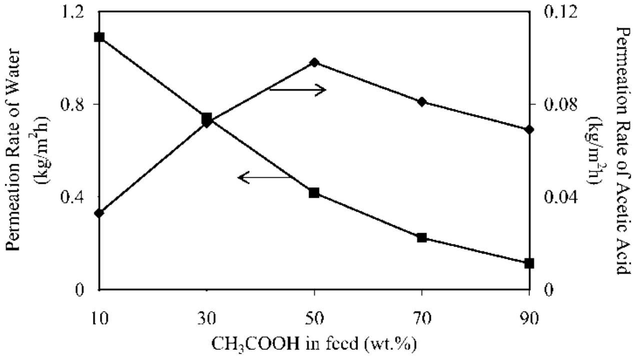

Figure 7. Variation of permeation rate of water (■) and acetic acid (◆) with feed composition.

acid content whereas the separation factor first decreased (70–80 wt.% acetic acid) and the increased with the acetic acid content.

In the study of Aminabhavi and coworker (36), in which PVA-g-AAm membranes were used to separate of water-acetic acid mixtures, the same trend was observed for the effect of feed composition on the permeation rate and the separation factor.

The results of the studies reported in the literature on the separation of acetic acid-water mixtures were listed in Table 3 for comparison purposes. As can be seen from the table, AN and HEMA grafted PVA membranes have high permeation rates and reasonable separation factors compared to the other grafted membranes.

The pervaporation separation index values were also calculated and shown in Fig. 9. The PSI value decreases monotonously until 70 wt.% acetic acid

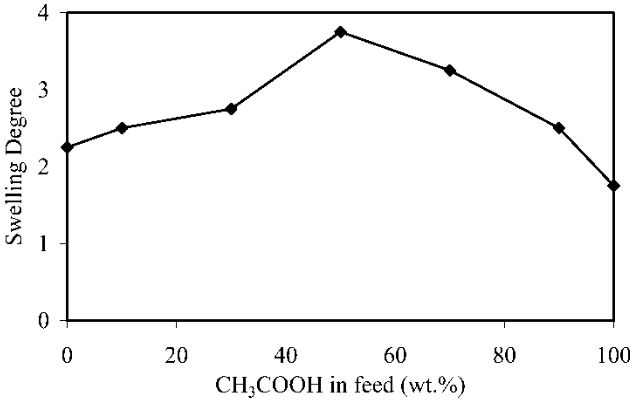

Figure 8. Change of degree of swelling with feed composition.

content and then increases. It can be concluded that the PVA-g-AN/HEMA membranes are suitable especially at low acetic acid concentrations.

Diffusion Coefficients

Molecular transport in pervaporation separation can be explained using solution-diffusion model (27). Diffusive transport occurs as a result of the concentration gradient and it is important to estimate the diffusion coefficient (D_i), to understand the transport mechanism. From the pervaporation results D_i was calculated using the following equation (8, 17, 33, 36, 37):

$$J_i = P_i[p_{i(\text{feed})} - p_{i(\text{permeate})}] = \frac{D_i}{h}[C_{i(\text{feed}} - C_{i(\text{permeate})}] \qquad (8)$$

Here, D_i is assumed to be constant across the effective membrane thickness (wet), *h*; $C_{i(\text{feed})}$ and $C_{i(\text{permeate})}$ are the mixture concentrations in the feed and permeate, respectively. The computed values of D_i (where subscript i stands for water or acetic acid) at 30°C are presented in Table 4. Values of D_i for water are quite higher than those observed for acetic acid at all feed compositions, suggesting that the membrane in this study is more water selective than acetic acid. As expected the diffusion coefficients of water and acetic acid decrease as the amount of acetic acid in the feed mixture increases. These results are also in agreement with the pervaporation results. Diffusion coefficients for 20 wt.% acetic acid in the feed mixture at different temperatures are presented in Table 5. The effect of temperature on D_i for water and acetic acid is also

Table 3. Comparison of the performance of the membranes used in the pervaporation separation of acetic acid-water mixtures which were based on PVA grafted with different monomers

Polymer	Feed Composition (%) (w/w)	Temperature (°C)	Permeation rate (J) (kg/m^{2}h)	Separation factor (α)	Reference
PVA-g-AAm (48%)	10–90	35	0.0303–0.5837	4.33–8.53	(36)
PVA-g-AAm (93%)	10–90	35	0.0621–0.8759	2.57–5.63	(36)
PVA-g-IA (10%)	20–90	40	0.005–0.740	66–119	(39)
PVA-g-AN(52%)	10–90	30	0.087–0.383	1.99–14.60	(19)
PVA-g-AN/HEMA	10–90	30	0.182–1.123	3.64–14.60	This study

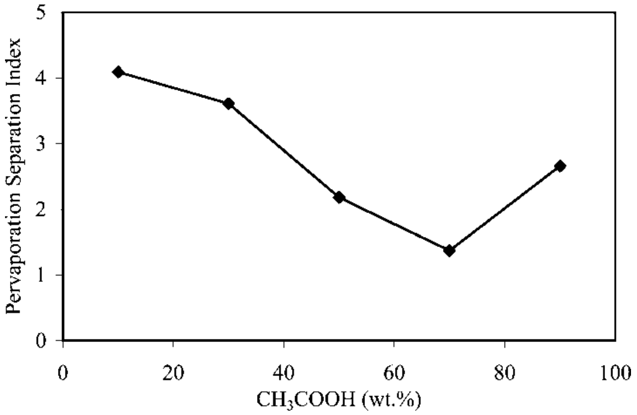

Figure 9. Change of PSI with feed composition.

systematic, as expected. An increase in the feed temperature increases the D_i values of both the water and the acetic acid.

The temperature dependency of the permeation rate and diffusion constant has been analyzed with the following Arrhenius relationships:

$$J_p = J_{po} \exp(-E_p/RT) \tag{9}$$

$$D_i = D_{io} \exp(-E_d/RT) \tag{10}$$

where E_d and E_p are the energies of activation for diffusion and permeation, respectively; J_{po} and D_{io} are the permeation and diffusion rate constants, respectively; R is the gas constant; and T is the temperature (K). Arrhenius plots of $\ln J_p$ and $\ln D_i$ versus $1/T$ are presented in Fig. 10 and Fig. 11 respectively. In all cases, straight lines are obtained, signifying the validity of the Arrhenius equation. The results of E_d and E_p were calculated from the slopes of the lines by the least squares method. These data are presented in Table 6. If the activation energy (E_p) is positive, J_p increases with increasing temperature; a phenomenon that is most common in pervaporation separation experiments. Similar results were found in the literature (37, 38). This further

Table 4. Diffusion coefficients of water and acetic acid calculated from eq. (8) at 30°C

wt.% CH_3COOH	$D_{water} \times 10^6$ (cm^2/s)	$D_{acetic\ acid} \times 10^7$($cm^2/s$)
10	4.30	1.30
30	1.07	1.04
50	0.56	1.32
70	0.23	0.82
90	0.06	0.37

Table 5. Diffusion coefficients of water and acetic acid calculated from eq. (8) at different temperatures for 20 wt.% acetic acid

Temperature (°C)	$D_{water} \times 10^6$ (cm^2/s)	$D_{acetic\ acid} \times 10^7$ (cm^2/s)
25	1.64	0.89
30	1.91	1.07
40	4.33	3.57
50	6.97	4.86

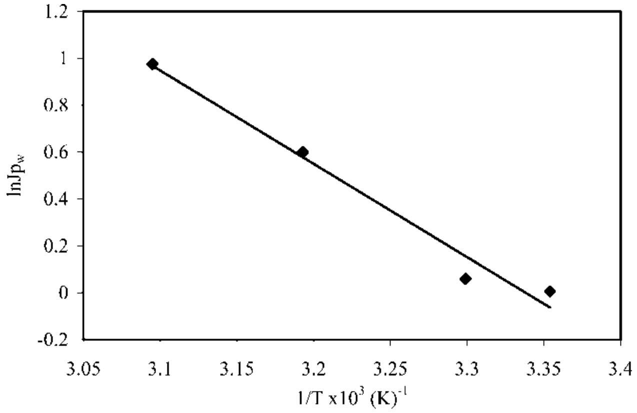

Figure 10. Arrhenius plot of $\ln J_P$ vs. $1/T$ for grafted PVA membrane.

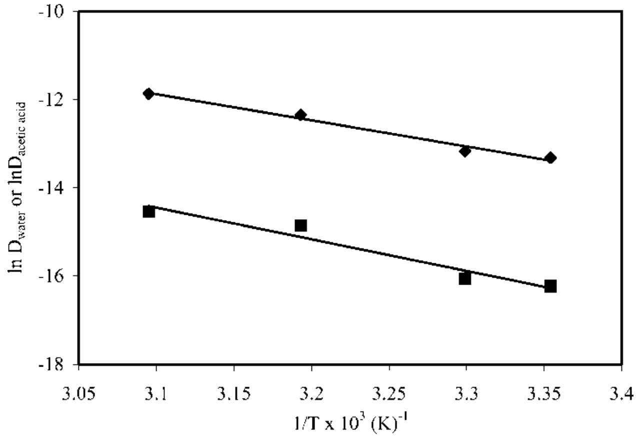

Figure 11. Arrhenius plot of $\ln D_{water}$ (■) and $\ln D_{acetic\ acid}$ (◆) vs. $1/T$ for grafted PVA membrane.

Table 6. Permeation and diffusion activation energies, and heat of sorption for water

Arrhenius activation parameters of PVA-g-AN/HEMA membrane	
E_P (kj/mol), eq. (9)	33.07
E_d(kj/mol), eq. (10)	49.27
ΔH_S (kj/mol)	−16.2

increases the driving force for mass transport because it represents the concentration gradient due to the differential vapor pressure of the permeate molecules between feed and permeate mixture. With the calculated values of E_p and E_d for water, the heat of sorption (ΔH_s) for water permeation has been calculated ($\Delta H_s = E_p - E_d$), and this data is also included in Table 6. The ΔH_s value is negative for the grafted PVA membrane, suggesting that sorption follows an endothermic process.

CONCLUSIONS

PVA-g-AN/HEMA membranes have been prepared and used in the pervaporation separation of acetic acid-water mixtures. It was shown experimentally that grafted PVA membranes could be used to separate acetic acid-water mixtures with acceptable permeation rates and separation factors. Separation factors of PVA membranes for acetic acid-water mixtures were enhanced by grafting with AN and HEMA.

The temperature dependency of the permeation rate, the separation factor, and the diffusion coefficient followed the Arrhenius trend. Increase in the feed temperature increased the permeation rate and diffusion coefficient of both water and acetic acid however decreased the separation factor in the temperature range of 25–50°C.

As the membrane thickness increased, the permeation rate decreased, whereas the separation factor increased up to the membrane thickness of 50 μm, and then stayed almost constant.

The grafted PVA membranes were found to be suitable in the pervaporation separation of acetic acid-water mixtures especially at low acetic acid concentrations.

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