

Notes

**STUDY OF COMPOSITE MEMBRANE OF CELLULOSE ACETATE OR
POLYVINYL ALCOHOL BLENDED WITH METHYLMETHACRY-
LATE-ACRYLIC ACID COPOLYMER FOR PERVAPORATION
SEPARATION***

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Abstract In this paper, methylmethacrylate-acrylic acid MMA-AA hydrophilic and hydrophobic copolymers were prepared by copolymerization for preparing membrane materials. The composite membrane of cellulose acetate (CA) blended with MMA-AA hydrophobic copolymer was used for the separation of methanol from pentane-methanol mixture. When the methanol concentration was only 1 wt%, the permeate flux still maintained at 350 g/m²h and separation factor was as big as 800. The composite membrane of PVA (polyvinyl alcohol) blended with MMA-AA hydrophilic copolymer was used for the separation of ethanol-water mixture. The permeate flux was increased to 975 g/m²h at 74°C and the separation factor reached 3000 at 25°C. The PVA/MMA-AA blended membrane surface modified by ammonia plasma was also investigated for separating ethanol-water mixture. Both permeate flux and separation factor of the membrane was improved. However, there was no obvious difference of plasma treatment time in the interval of 20~40 min.

Keywords Blended membranes, MMA-AA copolymers, Pervaporation separation of mixed solvents

INTRODUCTION

Pervaporation is an attractive separation technique for dehydration of organic solvents, removal of organic volatile compounds from water and separation of organic-organic mixtures. Today, about 100 industrial pervaporation plants of different sizes are in operation for dehydration of organic solvents^[1]. Recently, intensive investigations were conducted to develop effective pervaporation membranes for the separation of organic-organic mixtures^[2-4], such as separation of aromatics from aliphatic compounds and alcohol from alcohol-alkane mixtures.

In this paper, the membranes of PVA (polyvinyl alcohol) blended with hydrophilic MMA-AA copolymer and of CA blended with hydrophobic MMA-AA copolymer were prepared. The pervaporation characteristics of CA/MMA-AA membrane for separating methanol from methanol-pentane mixture and PVA/MMA-AA membrane for dehydrating aqueous alcohol solution with azeotropic concentration were investigated. The PVA/MMA-AA membrane with surface modified by ammonia plasma was also investigated for dehydrating aqueous ethanol solution.

EXPERIMENTAL

The copolymers of MMA-AA were prepared in our laboratory. Both hydrophilic and hydrophobic

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MMA-AA copolymers have a molecular weight of 0.22 million. The PAN (polyacrylonitrile) ultrafiltration membrane used as a support material was supplied by the Water Treatment Technology Center, Hangzhou. All solvents were of reagent grade. Both polymers, PVA and CA, were obtained from the Shanghai Chemical Reagent Supply Station.

The blended composite membranes were prepared by the following steps. 20% hydrophilic MMA-AA copolymer and 8% PVA aqueous solution were mixed together in various proportions for at least 48 h to form a homogeneous casting solution. This solution was cast onto the PAN support membrane. Then the PVA/MMA-AA blended membrane was dried at about 40°C for 3 h. By similar steps, the CA/MMA-AA blended membrane can also be prepared. The only difference is that the solvent used 8% hydrophobic MMA-AA polymer and 8% CA in acetone respectively and the blended membrane prepared was dried at room temperature for 20 min.

The pervaporation experiments were conducted with the equipment as reported previously^[5]. The vacuum system of the downstream side was maintained at 200–532 Pa. The experiments were carried out in a continuous steady state, operated at constant temperature of 15, 25, 35 and 45°C for methanol-pentane mixture and 25, 50 and 75°C for ethanol-water mixture. The permeate was condensed by liquid N₂.

The permeate flux and separation factors for all membranes were calculated according to previous report^[6].

RESULTS AND DISCUSSION

CA/MMA-AA Blended Composite Membrane for Separation of Methanol-Pentane Mixture

Figures 1 and 2 show the separation characteristics of three kinds of composite membrane as a function of methanol concentration in the mixture. For both CA membrane and MMA-AA membrane, the methanol permeated preferentially through these membranes. However, CA membrane has higher separation factor, and smaller permeate flux. On the contrary, MMA-AA membrane gives higher permeate flux, but lower separation factor.

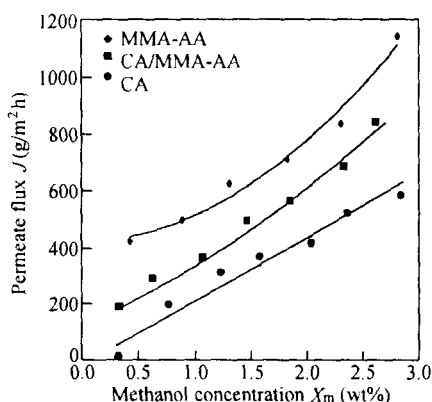


Fig. 1 The flux of CA/MMA-AA membrane (blend ratio 1:1) as a function of feed concentration

$T = 25^\circ\text{C}$, $P_{\text{up}} = 0.36 \text{ MPa}$, $P_{\text{dw}} = 532 \text{ Pa}$

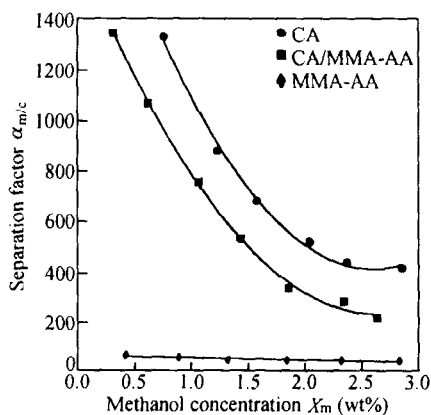


Fig. 2 The separation factor of CA/ MMA-AA membrane (blend ratio 1:1) as a function of feed concentration

$T = 25^\circ\text{C}$, $P_{\text{up}} = 0.36 \text{ MPa}$, $P_{\text{dw}} = 532 \text{ Pa}$

When CA membrane was blended with MMA-AA, its separation properties can be improved. The influence of blend ratio on the membrane separation properties is shown in Table 1. The results show that when blend ratio of CA and MMA-AA copolymer is 1:1, the separation properties are quite good.

Table 1. The influence of blend ratio on the membrane separation properties

Blend ratio (wt%) (CA:MMA-AA)	Flux (methanol) (g/m ² h)	Separation factor ($\alpha_{m/c}$)
1:0	535.4	420
2:1	630.7	312.5
1:1	758.2	245
1:2	824.9	120
0:1	950.3	39

Separation condition: $T = 25^{\circ}\text{C}$, $P_{\text{dw}} = 532\text{ Pa}$, $X_m = 2.5\text{ wt\%}$

From Figs. 1 and 2, we found that when the methanol concentration is 0.32%, the flux of CA/MMA-AA blended composite membrane for methanol is maintained at about 200 g/m² h and the separation factor reaches over 1300. That means that the CA/MMA-AA blended composite membrane has an acceptable separation factor and flux for separation of methanol from methanol-pentane mixture.

Figures 3 and 4 show the influence of operating temperature on the separation properties of membrane. For all the three composite membranes, their permeate flux increases with increasing operating temperature, but the separation factor decreases. Also, among these membranes the CA/MMA-AA blended membrane possesses the acceptable separation characteristics. Using this membrane, the pervaporation process can be produced at the room temperature.

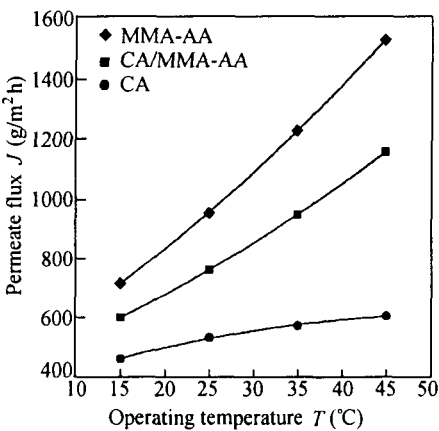


Fig. 3 The flux of CA/MMA-AA membrane (blend ratio 1:1) as a function of operating temperature
 $X_m = 2.5\%$, $P_{\text{up}} = 0.36\text{ MPa}$, $P_{\text{dw}} = 532\text{ Pa}$

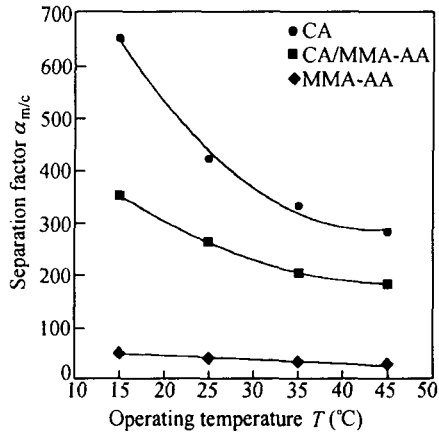


Fig. 4 The separation factor of CA/MMA-AA membrane (blend ratio 1:1) as a function of operating temperature
 $X_m = 2.5\%$, $P_{\text{up}} = 0.36\text{ MPa}$, $P_{\text{dw}} = 532\text{ Pa}$

PVA/MMA-AA Blended Membrane for Dehydration of Ethanol-Water Mixture

Figures 5~7 show the influence of blend ratios and amount of cross-linking agent on the separation characteristics of membranes, where C is the concentration of ethyleneglycol monomethacrylate used as a cross-linking agent during MMA-AA polymerization process. The amount of cross-linking agent added was about 2%, 4% and 8% respectively for MMA-AA copolymer. Ethanol-water mixture with azeotropic concentration was used in this experiment. The blend ratios for the membrane were 99/1 and 85/15, respectively.

Figure 8 showed the influence for plasma treatment time on the membrane separation characteristics. The blend ratio for this membrane was set at 85/15. The treatment condition for ammonia plasma was that the ammonia flow rate and discharge power was set at 60 mL/min and 90 W, respectively. In comparison with Fig. 6, both permeate flux and separation factor improved after the surface of the PVA/MMA-AA blended membrane was modified by ammonia plasma. It

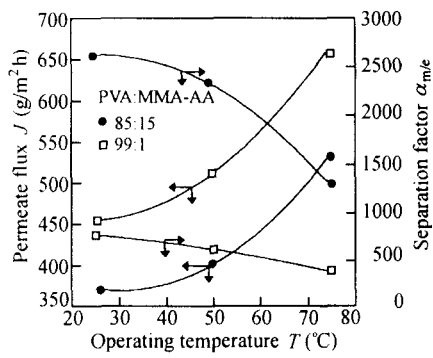


Fig. 5 The influence of operating temperature on separation factor and flux of PVA membrane $C=2\%$, $P_{up}=0.1$ MPa, $P_{dw}=532$ Pa

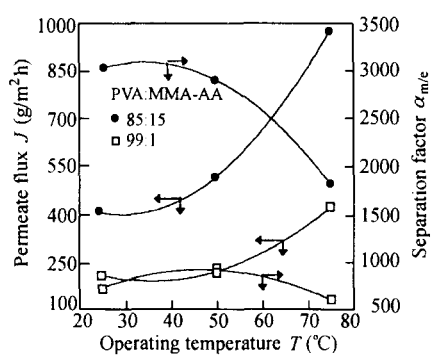


Fig. 6 The influence of operating temperature on separation factor and flux of PVA membrane $C=4\%$, $P_{up}=0.1$ MPa, $P_{dw}=532$ Pa

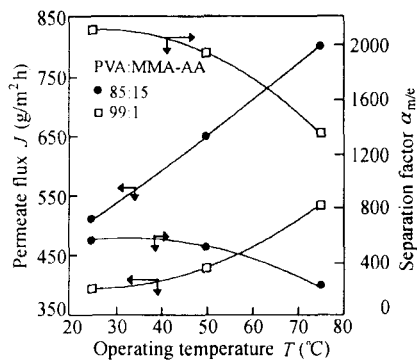


Fig. 7 The influence of operating temperature on separation factor and flux of PVA membrane $C=8\%$, $P_{up}=0.1$ MPa, $P_{dw}=532$ Pa

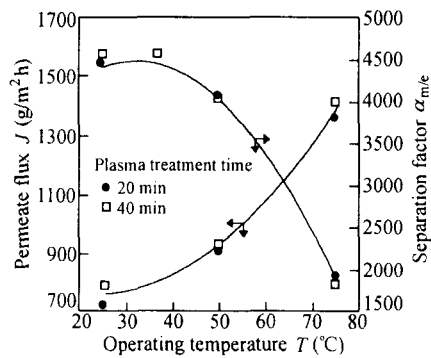


Fig. 8 The separation factor or flux as a function of operating temperature
Surface of the membrane treated by ammonia plasma, $C=4\%$

was also found that there was no obvious difference in the plasma treatment time in the interval of 20 ~ 40 min.

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