# Pervaporation properties of polyvinyl alcohol/ceramic composite membrane for separation of ethyl acetate/ethanol/water ternary mixtures

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**Abstract**–In further purification of ethyl acetate (EAC) process, azeotropic distillation or extractive distillation is usually applied. High energy consumption limits the economic profit of the process. In this study, pervaporation separation of EAC/ethanol (EA)/water ternary mixtures using the ceramic-supported polyvinyl alcohol (PVA) composite membrane was investigated to substitute the azeotropic distillation or extractive distillation. Swelling experiments were performed to evaluate the sorption characteristic of the membrane. Flory-Huggins theory was applied to study the interaction between the membrane and the penetrant. The UNIFAC model was adopted to investigate the variation of the penetrant activity in the membrane. The effects of operation temperature, feed water content and feed flow rate on the PV performance of the membrane were systematically investigated. The composite membrane exhibited high PV performance with the total flux of 2.1 kg·m$^{-2}$·h$^{-1}$ and 94.9 wt% permeate concentration of water (operation condition: feed composition 82.6 wt% EAC, 8.4 wt% EA, 9 wt% water, feed temperature 60 °C, feed flow rate 252 mL· min$^{-1}$). The PV performance of the membrane varied slightly over a continuous PV experiment period of 110 h. Our results demonstrated that the PVA/ceramic membrane was a potential candidate for the purification of EAC/EA/water ternary mixtures.

Key words: PVA/Ceramic Composite Membrane, Pervaporation, Ethyl Acetate, Ethanol, Water

## INTRODUCTION

Ethyl acetate (EAC) is an important solvent primarily used in industrial varnishes, thinners and nitrocellulose lacquers [1]. During the purification process of EAC, there are several binary and ternary azeotropes to be separated. Ordinary distillation is not suitable to separate the azeotrope. Thus, azeotropic distillation or extractive distillation is always necessary [2]. However, high energy consumption and capital cost of the two processes limit the economic profit of EAC. In addition, the product is easily to be contaminated due to the addition of entrainers or extractants. For a few decades, pervaporation (PV) has been considered as one of the most effective and energy-saving processes for separation of azeotropic or closing-boiling-point mixtures [3-12]. Consequently, the introduction of PV to replace azeotropic distillation or extractive distillation will provide an energy-saving, environmentally friendly and a simple process for the purification of EAC.

Pervaporation dehydration of EAC/water mixtures has been investigated by some researchers [13-17]. However, in the real process of EAC production, the crude product was EAC/ethanol (EA)/water mixtures. The residue curve map of the EAC/EA/water system is shown in Fig. 1. There are three azeotropes besides the EAC/water azeotrope in the EAC/EA/water system, which resulted in a more complicated ester system. Consequently, it is important to investigate the PV separation of EAC/EA/water mixtures. To our knowledge, few works have reported PV separation of EAC/EA/water
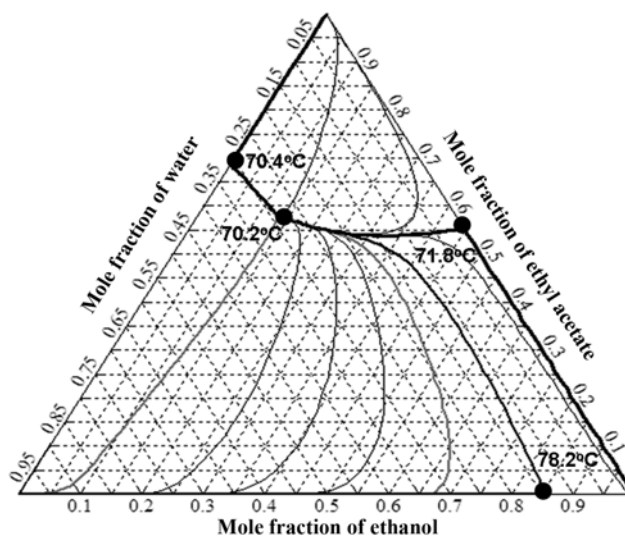


Fig. 1. Residue curve map of the EAC/EA/water system.

mixtures. Liu et al. [18] prepared the chitosan/poly (vinyl pyrrolidone) blend membranes for the PV dehydration of EAC/EA/water mixtures. They emphasized the preparation of the chitosan/poly (vinyl pyrrolidone) blend membranes but paid little attention to the process.

In our previous study [17,19], the ceramic-supported polyvinyl alcohol (PVA) composite membrane was prepared and applied in dehydration of EAC/water mixtures. It was found that the composite membrane had excellent PV performance in dehydration of EAC/ water mixtures. In this work, we further investigated the process of

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the PV separation of EAC/EA/water ternary mixtures using the ceramic-supported PVA composite membrane. Swelling experiments were performed to evaluate the sorption characteristic of the membrane. Flory-Huggins theory was used to calculate the interaction between the membrane and the penetrant. The influences of operation temperature, feed flow rate and feed composition on the PV performance of the membrane were analyzed. Furthermore, the long-term stability of the composite membrane in PV dehydration of EAC/EA/water ternary mixture was also studied.

## THEORY

According to the solution-diffusion model [20], the driving force of the PV process can be expressed by the gradient in chemical potential. The chemical potential at a given temperature and pressure can be expressed as the function of activity $a_i$:

$$\mu_i - \mu_i^0 = RT \ln a_i \tag{1}$$

When swelling equilibrium is reached at the interface between the mixture and the membrane, thermodynamic phase equilibrium between the mixture and the membrane is established, which indicates that the chemical potential of component i in each phase is equal.

$$\mu_i^f = \mu_i^m \tag{2}$$

Thus:

$$a_i^f = a_i^m \tag{3}$$

The activity of component i in the feed can be calculated by UNIFAC model [21]:

$$\ln a_i = \ln a_i^c + \ln a_i^R = \ln \gamma_i^c + \ln \gamma_i^R + \ln x_i \tag{4}$$

where $\gamma_i^c$ is the combinatorial activity coefficient of component i, $\gamma_i^R$ is the residual activity coefficient of component i, $x_i$ is the mole fraction of component i.

The combinatorial activity coefficient can be calculated by:

$$\ln \gamma_i^c = \ln \frac{\phi_i}{x_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^{n} x_j l_j \tag{5}$$

$$l_i = \frac{Z}{2} (r_i - q_i) - (r_i - 1) \tag{6}$$

where Z is the coordination number and usually taken equal to 10.0. $\phi_i$ and $\theta_i$ are the volume fraction and the surface fraction of component i, respectively.

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \qquad \theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{7}$$

$$q_i = \sum_{k=1}^{n} v_k^{(i)} Q_k \qquad r_i = \sum_{k=1}^{n} v_k^{(i)} R_k \tag{8}$$

where the parameters $R_k$ and $Q_k$ are the volume parameter and surface parameter of group k, respectively. $v_k^{(i)}$ is the number of group k in molecular i. $R_k$ and $Q_k$ used in this study [22] were listed in Appendix. A.

The residual activity coefficient can be calculated by:

**Table A1. Volume parameters and surface parameters**

| Group | $R_k$ | $Q_k$ |
|---|---|---|
| $H_2O$ | 0.920 | 1.400 |
| EA | 2.106 | 1.972 |
| $CH_2$- | 0.674 | 0.540 |
| $CH_3$- | 0.901 | 0.848 |
| $CH_3COO$- | 1.903 | 1.728 |

**Table B1. Interaction parameters of groups**

| Group | 1 $H_2O$ | 2 EA | 3 $CH_2$ | 4 $CH_3$ | 5 $CH_3COO$ |
|---|---|---|---|---|---|
| 1 $H_2O$ | 0 | −148.5 | 580.6 | 580.6 | −455.4 |
| 2 EA | 285.4 | 0 | −87.93 | −87.93 | 76.2 |
| 3 $CH_2$ | 1318 | 737.5 | 0 | 0 | 232.1 |
| 4 $CH_3$ | 1318 | 737.5 | 0 | 0 | 232.1 |
| 5 $CH_3COO$ | 1135 | 109.9 | 114.8 | 91.46 | 0 |

$$\ln \gamma_i^R = \sum_{i=1}^{n} v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^i] \tag{9}$$

where $\Gamma_k$ is the activity coefficient of group k, $\Gamma_k^{(i)}$ is the activity coefficient of group k in pure component i.

$$\ln \Gamma_k = Q_k \left[ 1 - \ln \left( \sum_{j=1}^{n} \overline{\theta}_j \psi_{jk} \right) - \sum_{j=1}^{n} \left( \frac{\overline{\theta}_j \psi_{kj}}{\sum_{p=1}^{n} \overline{\theta}_p \psi_{pj}} \right) \right] \tag{10}$$

$\psi_{jk}$ and $\psi_{kj}$ can be expressed as:

$$\psi_{jk} = \exp \left( -\frac{a_{jk}}{T} \right) \quad \psi_{kj} = \exp \left( -\frac{a_{kj}}{T} \right) \tag{11}$$

where $a_{jk}$ and $a_{kj}$ are the interaction parameters of group j and k. $a_{jk}$ and $a_{kj}$ used in this study [22] are listed in Appendix. B.

$$\overline{\theta}_j = \frac{Q_j X_j}{\sum_{p=1}^{n} Q_p x_p} \tag{12}$$

where $Q_j$ was the surface parameter of group j, $X_j$ is the fraction of group j in the liquid.

$$X_j = \frac{\sum_{i=1}^{c} v_j^{(i)} x_i}{\sum_{i=1}^{c} \sum_{k=1}^{n} v_k^j x_i} \tag{13}$$

where $v_j^{(i)}$ is the number of group j in component i.

## EXPERIMENTAL

### 1. Membrane Preparation

The preparation of PVA/ceramic composite membrane followed with our previous work [17]. 7 wt% PVA solution was prepared, maleic acid and sulfuric acid were used as crosslinking agent and catalyst, respectively. The resultant solution was coated onto the pretreated ceramic supports by dip-coating method. The prepared membranes were air dried and then annealed at 120 °C for 3 h.

### 2. Swelling Experiment

Samples of the active layer of the composite membrane were

weighted and immersed in pure water, EA and EAC at 60 °C, respectively. The weight of each sample was monitoring periodically until a constant weight was achieved. The swollen membranes were then removed from the solutions, rapidly blotted with tissue paper and then weighted immediately. The degree of swelling (Ds) was defined as:

$$Ds = \frac{W_w - W_d}{W_d} \times 100\% \tag{14}$$

where $W_w$ and $W_d$ are the weight of wet membrane and dry membrane, respectively.

## 3. Pervaporation Experiment

The pervaporation experiment was conducted on a homemade apparatus reported in our previous work [19,23]. The feed was circulated from the feed tank to the membrane module with a desired flow rate. A vacuum pump was applied to maintain the permeate pressure at less than 1,000 Pa. The penetrant was collected in a cold trap filled with liquid nitrogen. Permeate composition was determined by gas chromatography (GC-2014, SHIMADZU, Japan) equipped with a thermal conductivity detector (TCD) using a Porapak Q packed column and helium (He) as the carrier gas. The temperature of the injector, detector and oven was set at 180, 180 and 160 °C, respectively. The permeation flux of component i ($J_i$) and the separation factor was calculated according to the following equations:

$$J_i = \frac{W_i}{At} \tag{15}$$

where $W_i$ represents the weight of component i in the permeate (kg), A is the effective membrane area (m$^2$), t is the measurement time (h).

$$\alpha_i = \frac{y_{iP}/(1 - y_{iP})}{x_{iF}/(1 - x_{iF})} \tag{16}$$

where $y_{iP}$ and $x_{iF}$ represent the weight fraction of component i in permeate and feed, respectively.

## RESULTS AND DISCUSSION

### 1. Swelling Study

Swelling behavior of the membrane plays an important role in determining the PV performance of the membrane. The interaction between the permeate molecules and the membrane could well be determined by swelling experiment. In our previous work [19], Flory-Huggins theory was utilized to calculate the interactions of water with the membrane (Water-M), and EAC with the membrane (EAC-M). We found that Water-M played a more important role in the PV process. Consequently, in the present work, we further analyze the interaction of EA with the membrane (EA-M), Water-M and EAC-M.

According to Flory-Huggins theory [24], the interaction parameter of the penetrant and the membrane $\chi_{im}$ can be expressed as:

$$\chi_{im} = -\frac{[\ln(\phi_{im}) + (1 - \phi_{im})]}{(1 - \phi_{im})^2} \tag{17}$$

where $\phi_{im}$ is the volume fraction of component i in membrane which can be calculated by swelling experiment. Subscripts 1, 2, 3 and m denote water, EA, EAC and the membrane, respectively. The low-

**Table 1. The Ds and interaction parameters of the penetrants with the membrane**

|       | Ds (%) | $\chi_{im}$ |
|-------|--------|-------------|
| Water | 70.98  | 0.75        |
| EA    | 2.72   | 2.24        |
| EAC   | 0.23   | 4.54        |

est value of $\chi_{im}$ indicates the highest sorption level and thus the best affinity between the penetrant and the membrane.

The Ds and calculated interaction parameters of the penetrant with the membrane $\chi_{im}$ are given in Table 1. It can be seen that the Water-M was much more intensive than EA-M and EAC-M, indicating that the membrane has the best affinity for water. As shown in Table 1, the EA-M was more intensive than EAC-M. This may attributed to the fact that EA and EAC are both non- solvents of PVA, but the polarity of EA is more than that of EAC; thus, the membrane has better affinity for EA. Therefore, the affinity of the membrane to the penetrants was in the following order: Water>EA>EAC; the priority of sorption was in the following order: Water>EA>EAC.

## 2. Pervaporation Characterization

### 2-1. Effect of Feed EA Content

The activity of penetrant in the membrane was calculated by Eqs. (3)-(13). The influence of EA content in the feed (the water content in feed was kept at 9 wt%) on the activity of penetrant in the membrane is shown in Fig. 2. The activity of EA in the membrane increased while the activity of EAC in the membrane decreased with increasing EA content in the feed. This phenomenon indicated that the driving force of EA increased while that of EAC decreased with increasing EA content. In the meantime, the slight variation of water activity in the membrane suggested that the driving force of water changed slightly with EA content in the feed.

The influence of EA content in feed on the flux is illustrated in Fig. 3(a). The total flux increased slightly with increasing EA content. As pointed out by Chang et al. [25], the fluctuation and the flexibility of the chains were promoted by the presence of solvent in the membrane, which was beneficial to the transport of the penetrants. Thus, the flux increased with increasing EA content. As dis-
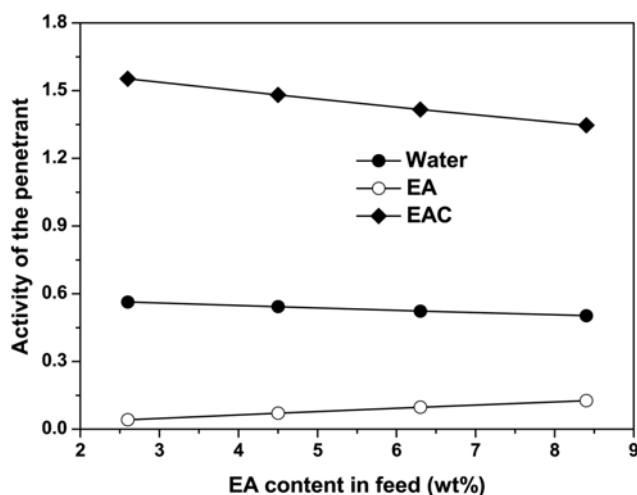


**Fig. 2. Effect of EA content in the feed on the activity of penetrant in the membrane.**
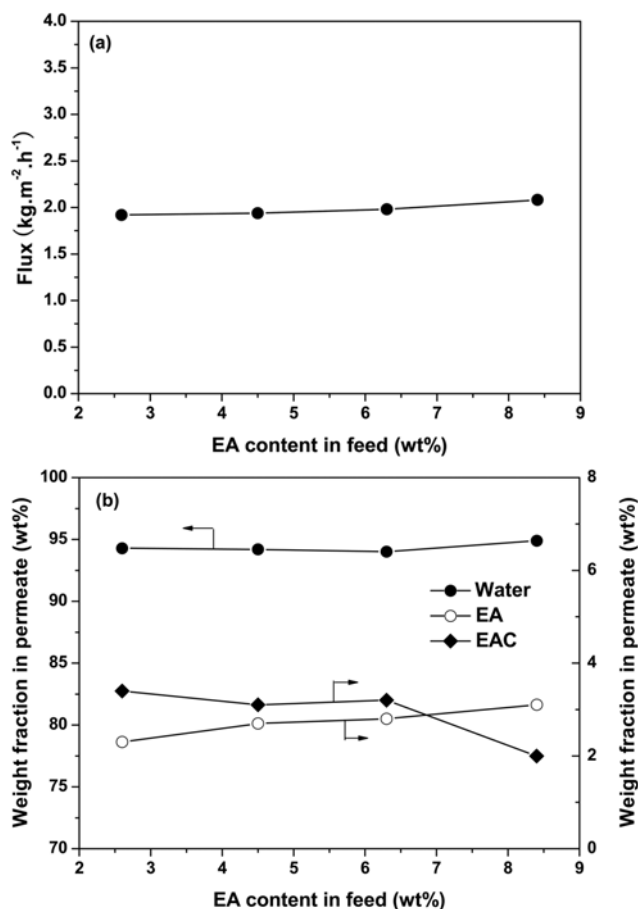
Fig. 3. Effect of EA content in the feed on (a) the total flux of the composite membrane, (b) the composition in the permeate (operation condition: feed temperature 60 °C, and the feed flow rate 252 mL·min⁻¹).
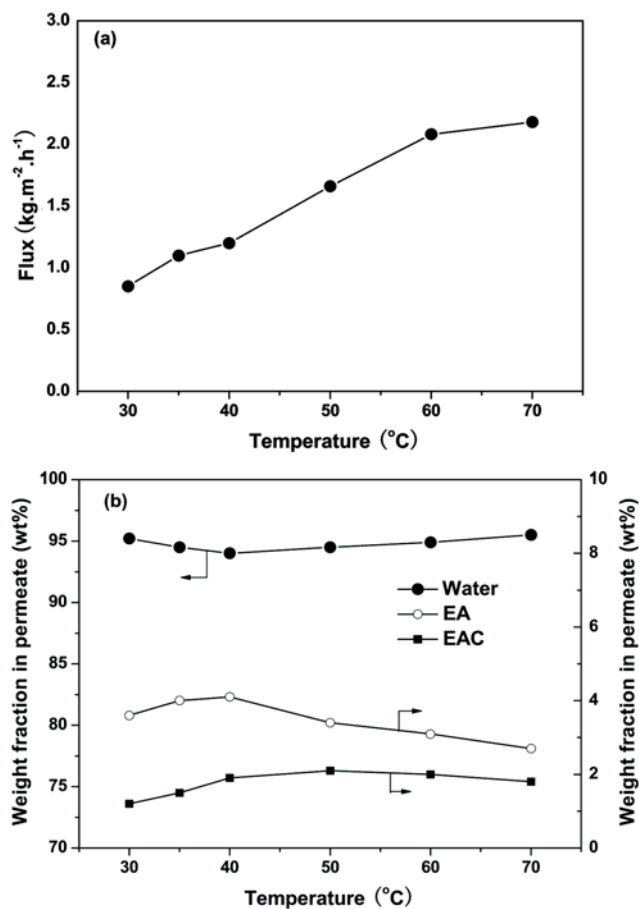


Fig. 4. Effect of feed temperature on (a) the total flux of the composite membrane, (b) the composition in the permeate (operation condition: feed composition 82.6 wt% EAC, 8.4 wt% EA, 9 wt% water and the feed flow rate 252 mL·min⁻¹).

than EA-M and EAC-M; thus Water-M played a more important role in PV process. The water content in feed was kept constant, resulting in the constant interaction between water and the membrane. In other words, the amount of water adsorbed in the membrane was constant. Furthermore, the activity of water in the membrane (as shown in Fig. 2) varied slightly and the driving force of water was almost constant; consequently, the flux increased slightly.

The effect of EA content on the permeate composition is shown in Fig. 3(b). The permeate concentration of water varied slightly attributed to the constant water content in feed. The permeate concentration of EA increased while that of EAC decreased with increasing EA content in feed. With EA content in feed increased, the activity of EA in the membrane increased (as shown in Fig. 2), resulting in the increase of the permeate concentration of EA. The decrease of the permeate concentration of EAC was attributed to the decrease of EAC activity in the membrane (as shown in Fig. 2). When the EA content in feed varied from 2.6 wt% to 6.3 wt%, the permeate concentration of EAC was higher than that of EA. Although, the affinity of the membrane to EA was better than that of the membrane to EAC, the amount of EA adsorbed into the membrane was less than EAC attributed to the low content of EA in feed. When EA in the feed was at a relatively high level, EA molecules adsorbing into the membrane was more than EAC molecules attrib-

uted to the better affinity of the membrane to EA. As a consequence, the permeate concentration of EA was more than that of EAC, and this condition was beneficial for the purification of EAC.

2-2. Effect of Operation Temperature

Operation temperature has a significant effect on the PV performance of the composite membrane. Fig. 4(a) shows the effect of operation temperature on the total flux of the membrane. The total flux increased significantly with increasing the temperature. When the temperature increased, the partial pressure of the components in the feed side increased. As a consequence, the driving force for mass transfer across the membrane increased, resulting in the increase of flux. In addition, high temperature accelerated the diffusion of the penetrants, which favored the mass transfer of the process, and thus the flux increased.

The influence of the operation temperature on the permeate composition is illustrated in Fig. 4(b). The permeate concentration of water decreased while that of EA and EAC increased as the temperature increased from 30 °C to 40 °C. When the the temperature increased from 30 °C to 40 °C, sorption dominated the diffusion. The sorption of water into the membrane decreased when the temperature increased from 30 °C to 40 °C, and accordingly, the permeate concentration of water decreased. However, when the temperature increased from 40 °C to 70 °C, the permeate concentration

of water increased while that of EA and EAC decreased. As the temperature varied from 40 °C to 70 °C, the rotating frequency and amplitude of the polymer chain increased, leading to increasing the free volume. Hence, the transport of water which has the smallest molecular dynamic diameter was accelerated. In the meantime, at this temperature range the diffusion dominated the sorption. The dynamic molecular diameters of the penetrants were in the following order: EAC>EA>water; consequently the diffusion rate of the penetrants was in the opposite order: water>EA>EAC. As a result, the amount of EAC and EA transported across the membrane was smaller than that of water. Thus, the permeate concentration of water increased while the permeate concentration of EAC and EA decreased with the temperature increased from 40 °C to 70 °C.

The temperature dependence of the flux J can be expressed by Arrhenius-type relation:

$$J = J_0 \exp(-E_p/RT) \tag{18}$$

where $J_0$ is the Arrhenius constant, $E_p$ is the activation energy for the permeation, R is the universal gas constant, and T is the absolute temperature.

Arrhenius plot of ln J versus 1/T is illustrated in Fig. 5. The relationship between ln J and 1/T indicated a good linearity in the given temperature range and the behavior of the composite membrane followed the Arrhenius law. The activation energy of the membrane was 20.4 kJ·mol$^{-1}$.

## 2-3. Effect of Feed Flow Rate

Fig. 6 illustrates the effect of the feed flow rate on the PV performance of the composite membrane. The total flux increased while the permeate composition varied slightly with increasing the feed flow rate. When the feed flow rate increased, the concentration polarization and the temperature polarization extent decreased. Hence, the mass transfer resistance decreased, which resulted in the increase of the total flux.

## 2-4. Long-term Stability

The stability of the membrane was an important factor in the PV process. Consequently, the PVA/ceramic composite membrane was tested in the pervaporation dehydration of EAC/EA/water ternary



Fig. 6. Effect of feed flow rate on (a) the total flux of the composite membrane, (b) the composition in the permeate (operation condition: feed composition 82.6 wt% EAC, 8.4 wt% EA, 9 wt% water and the feed temperature 60 °C).

mixture (82.6 wt% EAC, 8.4 wt% EA, and 9 wt% water) over a period of 110 h. As shown in Fig. 7, the flux and permeate concentration of water had little change during the operation time.
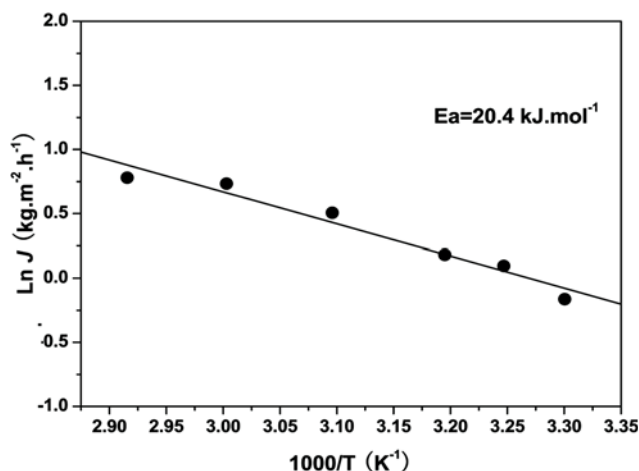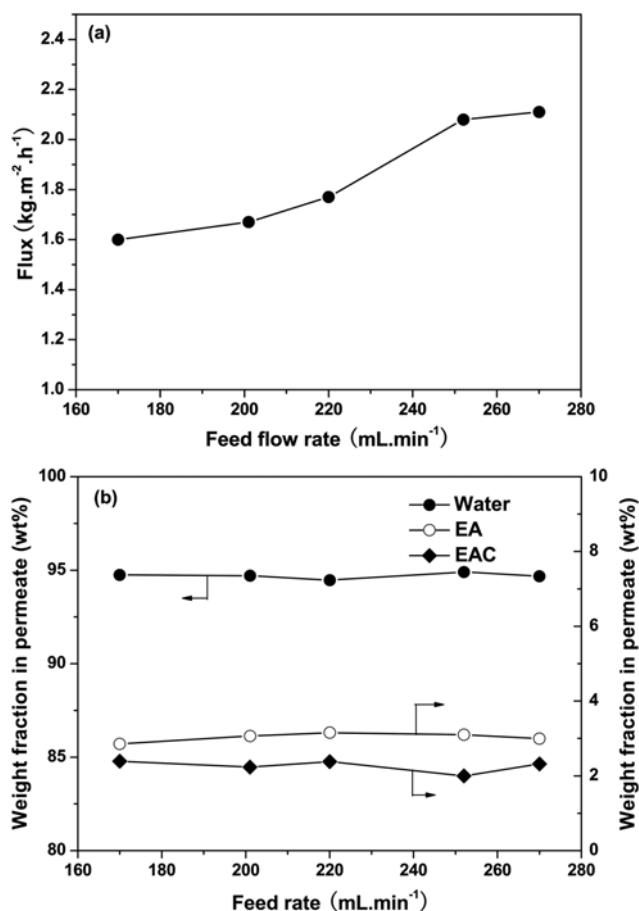


Fig. 5. The plots between the total flux of the composite membrane and the feed temperature reciprocal (operation condition: feed composition 82.6 wt% EAC, 8.4 wt% EA, 9 wt% water and the feed flow rate 252 mL·min$^{-1}$).
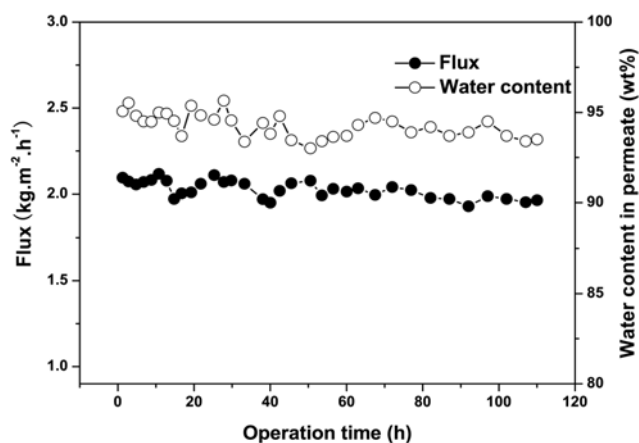


Fig. 7. Long-term stability of the composite membrane in the the pervaporation dehydration of EAC/EA/water mixture (operation condition: feed composition 82.6 wt% EAC, 8.4 wt% EA, 9 wt% water, the feed temperature 60 °C, and the feed flow rate 252 mL·min$^{-1}$).

**Table 2. Comparison of PV performance of the composite membrane with other published works**

| Membrane | Feed composition (wt%) | Temperature (°C) | Flux (g·m⁻²·h⁻¹) | Permeate concentration of water (wt%) | Ref. |
|---|---|---|---|---|---|
| PVA (crosslinked by TAC) | EAC/W=97.5/2.5 | 50 | 55 | 99.0 | [13] |
| Standard PVA (GFT) | EAC/HAC/W=40/50/10 | 65 | 46.7 | 88.9 | [14] |
| PFSA-TEOS/PAN | EAC/W=98/2 | 40 | 205 | 91.0 | [15] |
| PU | EAC/W=92/8 | 30 | 187 | 78.7 | [16] |
| CS/PVP blend membrane | EAC/EA/W=82.6/8.4/9 | 35 | 953 | 98.6 | [18] |
| PVA/ceramic | EAC/EA/W=82.6/8.4/9 | 35 | 1100 | 94.5 | This work |
| PVA/ceramic | EAC/EA/W=82.6/8.4/9 | 60 | 2100 | 94.9 | This work |

EAC: ethyl acetate, EA: ethanol, HAC: acetic acid, W: water, PU: poly-urethane

The PVA/ceramic composite membrane exhibited high PV performance (the flux was 2.1 kg·m⁻²·h⁻¹ and the permeate concentration of water was 94.9 wt%) in separation of water/EA/EAC ternary mixtures with the feed flow rate of 252 mL·min⁻¹ and operation temperature of 60 °C. Comparison of the PV performance of the composite membrane with other published works is illustrated in Table 2. The PVA/ceramic composite membrane exhibited high PV performance in the PV separation of EAC/EA/water mixtures. The high performance of the PVA/ceramic composite membrane in our work could greatly meet the requirement of commercial production.

## CONCLUSIONS

PV separation of EAC/EA/water ternary mixtures was performed using the ceramic-supported PVA composite membrane. Flory-Huggins theory was applied to study the interaction between the membrane and the penetrant. The interaction of the membrane and the penetrant was in the following order: Water>EA>EAC. The effects of operation temperature, feed water content and feed flow rate on the PV performance of the membrane were systematically investigated. When EA in the feed was at a relatively high level, the permeate concentration of EA was more than that of EAC, which was favorable to the purification of EAC. When the operation temperature was 60 °C, the feed flow rate was 252 mL·min⁻¹ and the feed solution was 82.6 wt% EAC/8.4 wt% EA/9 wt% water, the composite membrane exhibited high PV performance (the total flux was 2.1 kg·m⁻²·h⁻¹ and the permeate concentration of water reached 94.9 wt%). The PV performance of composite membrane changed slightly during 110 h continuous PV experiment. This work provides a promising process for the purification of EAC.

## NOMENCLATURE

$J_i$ : permeation flux of component i
$W_i$ : weight of component i in the permeate

A : effective membrane area
t : measurement time
$x_{iF}$ : fraction of component i in feed
$y_{iP}$ : fraction of component i in permeate
Z : coordination number
R : universal gas constant
$a_i$ : activity of component i
$a_{jk}$ : interaction parameter of group j and k
$x_i$ : mole fraction of component i.
$R_k$ : volume parameter of group k
$Q_k$ : surface parameter of group k
$X_j$ : fraction of group j in the liquid
Ds : degree of swelling
$W_w$ : weight of wet membrane
$W_d$ : weight of dry membrane
T : absolute temperature

**Greek Letters**

$\alpha_i$ : separation factor
$\mu_i$ : chemical potential of component i
$\gamma_i^c$ : combinatorial activity coefficient of component i
$\gamma_i^R$ : residual activity coefficient of component i
$\phi_i$ : volume fraction of component i
$\theta_i$ : surface fraction of component i
$v_k^{(i)}$ : the number of group k in molecular i
$\Gamma_k$ : activity coefficient of group k
$\Gamma_k^{(i)}$ : activity coefficient of group k in pure component i
$v_j^{(i)}$ : number of group j in component i
$\chi_{im}$ : interaction parameter of composite i with the membrane
$\phi_{im}$ : volume fraction of component i in membrane

**Subscript**

i, j : component i, j
1 : water
2 : ethanol
3 : ethyl acetate
m : membrane

## REFERENCES

1. P. Dutia, *Chemical Weekly-Bombay-.*, **49**, 176 (2004).
2. A. Szanyi, P. Mizsey and Z. Fonyo, *Ind. Eng. Chem. Res.*, **43**, 8269 (2004).

3. X. Feng and R. Y. M. Huang, *Ind. Eng. Chem. Res.*, **36**, 1048 (1997).

4. P. D. Chapman, X. Y. Tan, A. G. Livingston, K. Li and T. Oliveira, *J. Membr. Sci.*, **268**, 13 (2006).

5. S. Sommer and T. Melin, *Chem. Eng. Process.*, **44**, 1138 (2005).

6. D. A. Devi, B. Smitha, S. Sridhar, S. S. Jawalkar and T. M. Aminabhavi, *J. Chem. Technol. Biotechnol.*, **82**, 993 (2007).

7. K. S. Chang, Y. H. Huang, K. R. Lee and K. L. Tung, *J. Membr. Sci.*, **354**, 93 (2010).

8. Z. M. Mao, Y. M. Cao, X. M. Jie, G. D. Kang, M. Q. Zhou and Q. Yuan, *Sep. Purif. Technol.*, **72**, 28 (2010).

9. L. Y. Jiang, T. S. Chung and R. Rajagopalan, *AIChE J.*, **53**, 1745 (2007).

10. J. H. Chang, J. K. Yoo, S. H. Ahn, K. H. Lee and S. M. Ko, *Korean J. Chem. Eng.*, **15**, 28 (1998).

11. H. S. Choi, S. D. Hong, G. J. Hwang, C. S. Park, K. K. Bae and K. Onuki, *Korean J. Chem. Eng.*, **23**, 288 (2006).

12. H. H. Nguyen, N. Jang and S. H. Choi, *Korean J. Chem. Eng.*, **26**, 1 (2009).

13. Y. Salt, A. Hasanoğlu, İ. Salt, S. Keleşer, S. Özkan and S. Dinçer, *Vacuum.*, **79**, 215 (2005).

14. H. I. Shaban, *J. Appl. Polym. Sci.*, **70**, 2361 (1998).

15. H. K. Yuan, Z. L. Xu, J. H. Shi and X. H. Ma, *J. Appl. Polym. Sci.*, **109**, 4025 (2008).

16. D. A. Devi, K. V. S. N. Raju and T. M. Aminabhavi, *J. Appl. Polym. Sci.*, **103**, 3405 (2007).

17. Y. X. Zhu, S. S. Xia, G. P. Liu and W. Q. Jin, *J. Membr. Sci.*, **349**, 341 (2010).

18. X. H. Zhang, Q. L. Liu, Y. Xiong, A. M. Zhu, Y. Chen and Q. G. Zhang, *J. Membr. Sci.*, **327**, 274 (2009).

19. S. S. Xia, X. L. Dong, Y. X. Zhu, W. Wei, F. J. Xiangli and W. Q. Jin, *Sep. Purif. Technol.*, **77**, 53 (2011).

20. J. G. Wijmans and R. W. Baker, *J. Membr. Sci.*, **107**, 1 (1995).

21. T. Oishi and J. M. Prausnitz, *Ind. Eng. Chem. Process Des. Dev.*, **17**, 333 (1978).

22. A. Fredenslund, J. Gmehling and P. Rasmussen, *Vapour-Liquid Equilibria Using UNIFAC*, Elsevier Science Publishers B V, Amsterdam (1977).

23. F. J. Xiangli, Y. W. Chen, W. Q. Jin and N. P. Xu, *Ind. Eng. Chem. Res.*, **46**, 2224 (2007).

24. M. H. V. Mulder and C. A. Smolders, *J. Membr. Sci.*, **17**, 289 (1984).

25. K. S. Chang, C. C. Hsiung, C. C. Lin and K. L. Tung, *J. Phys. Chem. B.*, **113**, 10159 (2009).