

# Studies on the PVA/P(AA-Co-AN/SiO<sub>2</sub>)/ PVA Composite Membranes for Pervaporation Dehydration of Methanol

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## Abstract

Acrylic acid (AA) and acrylonitrile (AN) were synthesized by solution polymerization with nanometer SiO<sub>2</sub>. The copolymer solution was made into main body of the membranes, then composited with the polyvinyl alcohol (PVA) acetal membranes, to make the three-layer sandwich composite pervaporation membranes. The adsorption and the preferential sorption characteristics of the membranes were analyzed by studying swelling degree in different concentrations of methanol solution. Furthermore, the structure unit ratios of the P(AA-Co-AN/SiO<sub>2</sub>) membranes were analyzed by X-ray Photoelectron Spectroscopy (XPS). Pervaporation experiments were carried out using these membranes to separate methanol/water mixture, and results showed that selectivity of the membranes has increased with increasing the ratio of AN, but flux decreased. When the comonomer ratio AA/AN was 1/1, for the 98wt% mixtures at 60°C, the separate factor was up to 1534, and the permeation flux was 583 g/(m<sup>2</sup>·h). Moreover, the composite membranes also showed good stability by a long-term test of the pervaporation experiments.

**Keywords:** Methanol/water mixture, Acrylic acid (AA)/acrylonitrile (AN), Pervaporation, Composite membranes

## 1. Introduction

Pervaporation is recognized as one of the rapidly developing and promising technologies for the dehydration of organic liquids in various industrial processes. Especially, it is effective in separating azeotropic and close boiling liquid mixtures (Gimenes et al., 2007, pp.71-79; Veerapur et al., 2007, pp.102-111) that are difficult to separate by conventional distillation. In addition, it is safe to handle the heat-sensitive and hazardous compounds (Anjali Devi et al., 2006, pp.45-53). Compared with conventional separation methods, pervaporation, an energy saving technology, is better candidate for dehydration purpose (Zhu et al., 2010, pp.341-348).

The dehydration of organic solvents is the most important application of pervaporation. The first commercial application of the pervaporation process was the dehydration of ethanol, using a hybrid system with a distillation column. Dehydration of acetic acid by hydrophilic membranes like acrylonitrile and hydroxy ethyl methacrylate grafted poly(vinyl alcohol) membrane has already been commercialized. The pervaporation unit can also be used in combination with a reaction, where it constantly removes one of the reaction products to shift the equilibrium reaction to higher yields.

Since the dewatering of organic solvents, dehydration of low molecular weight alcohols is the most common application. There are many publications on the separation of ethanol/water mixtures (Kim et al., 2000, pp.83-93; Kuhn et al., 2009, pp.261-274; Nomura et al., 1998, pp.161-171; Vane et al., 2008, pp.230-241). However, it is

nearly no study and application on separating methanol/water mixture. Compared with ethanol, methanol is more similar with water in polarity and molecular weight which makes methanol to compete with water on adsorbing in the membrane. So the pervaporation membrane which is available for separating ethanol/water mixture is not ideal for separating methanol/water mixture (Wesslein et al., 1990, pp.169-179).

In this work, acrylic acid (AA) and acrylonitrile (AN) were synthesized by solution polymerization with nanometer SiO<sub>2</sub>. The copolymer solution was made into main body of the membranes, then composited with the polyvinyl alcohol acetal membranes, to make the three-layer sandwich composite pervaporation membranes. The optimal content of nanometer SiO<sub>2</sub> in membranes had been investigated in previous work (Liu et al., 2008, pp.192-198). In this paper, the performance of the membranes with different AA/AN ratio was studied. Pervaporation experiments were carried out using these membranes to separate the mixtures of methanol/water over the complete concentration range 70–98wt%. The effect of membranes composition, feed temperature and feed concentration on the separation performance was investigated. When the comonomer ratio was 1/1, for the 98wt% mixtures at 60°C the separate factor was up to 1534, and the permeate flux was 583 g/(m<sup>2</sup>·h).

## 2. Experiments

### 2.1 Materials

Analytical reagent (A.R) grade of methanol, formaldehyde, potassium peroxodisulfate, N, N-methylene acrylamide came from the third Tianjin chemical reagent plant. A.R grade of AA monomer, AN monomer were obtained from Tianjin chemical reagent Ltd. PVA was obtained from Beijing organic chemistry company, the degree of polymerization is 1700, the degree of alcoholysis is 99%. Nanometer SiO<sub>2</sub> (TS-610) was bought from Cabot Corporation in America, and its average size is 70 nm.

### 2.2 Membrane preparing

PVA was dissolved in the deionized water coupled with a suitable 36wt% formaldehyde solution and adjusted the PH value to 2-3 using hydrochloric acid at 90°C, to prepare PVA acetal membrane solution. AA and AN were synthesized at the different monomer ratio by solution polymerization with nanometer SiO<sub>2</sub> using potassium peroxodisulfate as initiator and N,N-methylene acrylamide as cross-linking agent at 70°C to make the P(AA-Co-AN/ SiO<sub>2</sub>) membrane solution. First, PVA acetal membrane solution was scraped on the non-woven polyester fabric supporter as the first layer, and then under heat treatment at 75°C in the oven; Second, the P(AA-Co-AN/ SiO<sub>2</sub>) membrane solution as the middle layer of the composite membranes on the surface of the PVA acetal membranes; at last the PVA acetal membrane solution scraped on the surface of the P(AA-Co-AN/ SiO<sub>2</sub>) membranes went into the three-layer sandwich composite pervaporation membranes. The membranes were dried at 120°C for 1 h, and marinated in the deionized water and ethanol repeatedly to remove the dissolvable impurity.

### 2.3 Membranes prepared for pervaporation

Table 1 shows the P(AA-Co-AN/ SiO<sub>2</sub>) membranes compositions prepared by the method introduced in Section 2.2.

### 2.4 Copolymer (membrane) characterization

#### 2.4.1 Studies of degree of swelling

The prepared membrane samples were immersed in methanol/water mixture of different concentrations for at least 48h; membranes were weighed 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 degree of swelling (DS) was calculated by:

$$DS = \frac{M_w - M_D}{M_D} \times 100\% \quad (1)$$

Where M<sub>w</sub> is the mass of the swollen sample and M<sub>D</sub> is the dry mass.

#### 2.4.2 Studies of X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) was used to analyze the structure unit ratios of the P(AA-Co-AN/SiO<sub>2</sub>) membranes.

#### 2.4.3 Pervaporation studies

The apparatus used in this study is illustrated in Figure 1. The effective membrane area was 0.0127 m<sup>2</sup> and the

feed compartment volume was 250ml. Pervaporation experiments were conducted at constant temperatures ranging 40-90°C using different feed compositions.

The separation factor ( $\alpha$ ) for methanol is defined as:

$$\alpha = \frac{Y_{\text{H}_2\text{O}} / Y_{\text{MeOH}}}{X_{\text{H}_2\text{O}} / X_{\text{MeOH}}} \quad (2)$$

where  $X_{\text{H}_2\text{O}}$ ,  $X_{\text{MeOH}}$ ,  $Y_{\text{H}_2\text{O}}$ ,  $Y_{\text{MeOH}}$  are the weight fractions of water and methanol in the feed and in the permeate, respectively. Water is preferentially permeating component.

The permeation flux ( $J$ ) was determined by using the equation:

$$J = \frac{M}{A \times t} \quad (3)$$

where  $M$  is the weight of permeate, and  $A$  is the effective membrane area,  $t$  is the time of the experiment.

The pervaporation separation index (PSI) is calculated by using the following equation:

$$\text{PSI} = (\alpha - 1)J \quad (4)$$

where  $J$  and  $\alpha$  are the total permeation flux and separation factor, respectively.

### 3. Results and discussion

#### 3.1 Swelling properties

The pervaporation transport mechanism can generally be interpreted by the solution diffusion model. Thus, the preferential sorption characteristics of the membranes were explored. Water sorbed into a membrane is important for pervaporation dehydration because this affects the membrane permselectivity. Water sorbed by the hydrophilic groups results in the membrane swelling, assisting penetrants in diffusing through the membrane. However, too much water uptake by the membrane results in excessive swelling, mechanical fragility and morphological instability of the membrane.

Figure 2 shows the effect of comonomer ratio and feed methanol content on the DS of the membranes at 60°C. One can observe from Figure 2 that adding AN can depress the DS of the membrane. This can be attributed to the —CN group of AN which is hydrophobic group and can recede water sorbed of the membrane. From Figure 2, one can also find that all the membranes share a similar trend of the DS change. It was that DS of the membranes has decreased with increasing the methanol concentration. The cause is that PVA and AA are hydrophilic material. There many hydrophilic groups —OH in those molecule. So when increasing methanol concentration, the water concentration decreased and the less water can be sorbed in the membrane.

#### 3.2 XPS analysis

XPS analysis was used to mensurate the element content by which the ratio of —COOH/—CN in P(AA-Co-AN) membrane can be determined. Table 2 shows the XPS analysis results of different AA/AN ratio copolymer membranes and the separation performance of each composite membranes to 98 wt % methanol/water mixture.

One can observe from Table. 2 that adding AN has increased the —CN quality in the membranes and the separation factor, but the permeation flux decreased.

#### 3.3 Pervaporation studies

##### 3.3.1 Comparison between the membranes with different AA/AN ratio.

Different membranes are used for separating methanol/water mixture in 98wt%, and the results under different temperature are shown in Figure 3-5. Then, use the membranes to separate methanol/water mixture at different concentrations under 60°C. Fig.6-8 show the effect of feed concentration on the separation factor, flux and PSI to the different membranes.

Figure 3 shows the change of separation factor with the temperature increasing, Figure 4 shows the change of flux, and Figure 5 shows the change of PSI. In Figure 3, it can be found that the separation factors increase with AN content increasing. One can also find that all the membranes share a same trend of the separation factor change which has the top numerical value at 60°C. As shown in Figure 4 the permeation flux decrease with AN content increasing, but with the temperature increasing; the permeation flux is increasing too. This is because

increasing the —CN group of AN in membrane not only decrease water passed membrane but can also reject methanol through membrane effectively. It is shown in Figure 5 that the PSI has the similar trend with the separation factor. The membrane has a good pervaporation performance when the AA/AN ratio is 1/1 and the temperature is of 60°C.

As shown in Figure 6, with the feed concentration increasing, separation factors are increasing gradually, and beyond 85wt%, the change is greater. While in Figure 7, the flux is decreasing with the feed concentration increasing. This can be attributed to the swelling state of membranes. With the increase of methanol in the feed, membranes shrink gradually, and cause the free volume in the membrane to diminish, which lead to the flux decrease. It is obvious in Figure 8 that the PSI has the same trend with the separation factors with the feed concentration increasing.

The result can be received that the membrane has an encouraging separation performance with a flux of 583 g/(m<sup>2</sup>·h) and separation factor of 1534 at 60°C at the feed methanol content 98wt%.

### 3.3.2 Long-term test on the membrane

To investigate the stability of the separation performance of the membrane, a long-term test of the pervaporation was carried out for 48 hours using the membrane 3 in the table 1 to separate 98wt% methanol/water mixture under 60°C. The result was shown in the table 3.

From table 3, one can find that the separation performance of membrane has no considerable change in consecutive experiment. It testified that the prepared membrane has a good stability in separating methanol/water mixture at 60°C.

## 4. Conclusions

PVA/P(AA-Co-AN/SiO<sub>2</sub>)/ PVA composite membranes were prepared by varying the ratios of AA/AN of 2/1, 3/2, 1/1, 2/3 and 1/2 and used for PV separation of methanol/water mixtures. It demonstrates that the permeation flux increases with AN content increasing, however, separation factor shows the opposite trend. When the ratio of AA/AN was 1/1, the membrane has an encouraging separation performance with a flux of 583 g/(m<sup>2</sup>·h) and separation factor of 1534 at 60°C when the feed methanol content 98wt%. The long-term test of the pervaporation indicated that the membrane has a good stability in experiment condition.

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Table 1. The membranes ready for pervaporation

Name of the membranes	AA/AN (monomer)	The content of nanometer SiO <sub>2</sub> (wt%)
Membrane 1	2/1	0.1
Membrane 2	3/2	0.1
Membrane 3	1/1	0.1
Membrane 4	2/3	0.1
Membrane 5	1/2	0.1

Table 2. The XPS analysis results and the separation performance of different membranes

Name of the membrane	AA/AN	-COOH/-CN	$\alpha$	J/(g/(m <sup>2</sup> h))
Membrane 1	2/1	1/0.58	299.93	1016.04
Membrane 2	3/2	1/0.61	644.01	835.27
Membrane 3	1/1	1/0.81	1534.21	582.93
Membrane 4	2/3	1/1.15	1640.66	344.09
Membrane 5	1/2	1/1.66	1858.92	274.11

Table 3. The result of membrane under long-term test

Time (h)	$\alpha$	J g/(m <sup>2</sup> ·h)
2	582.93	1534.21
6	573.34	1562.32
12	559.23	1563.78
24	560.42	1590.56
48	542.42	1567.29

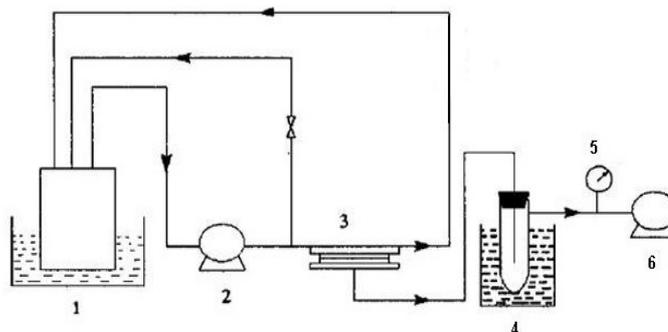


Figure 1. Schematics of pervaporation test equipment.(1) Feed flask, (2) transporting pump, (3) pervaporation pool, (4) cold trap, (5) vacuum meter, (6) vacuum pump.

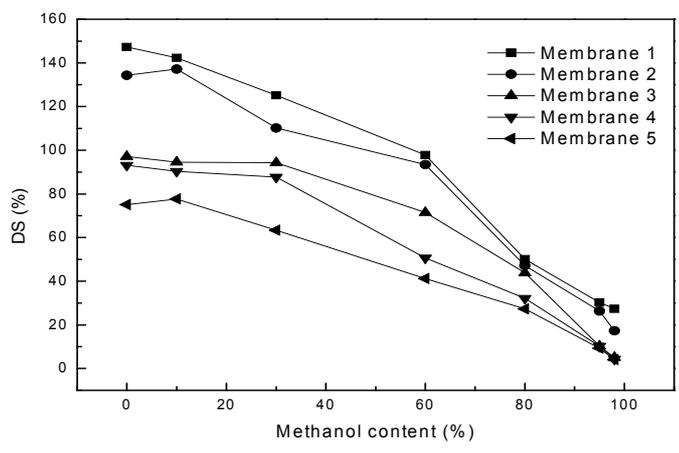


Figure 2. Effects of feed methanol content on DS of membranes

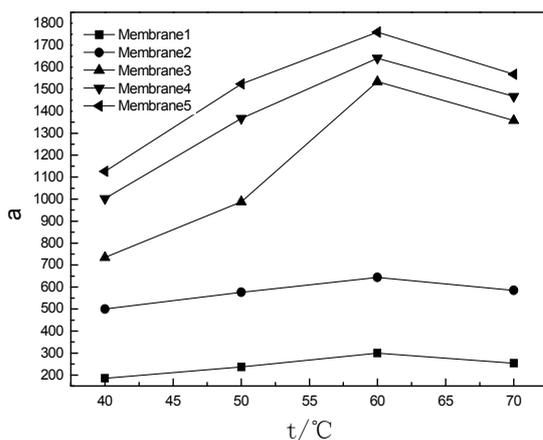


Figure 3. Comparison of different membrane separation factor under different temperature

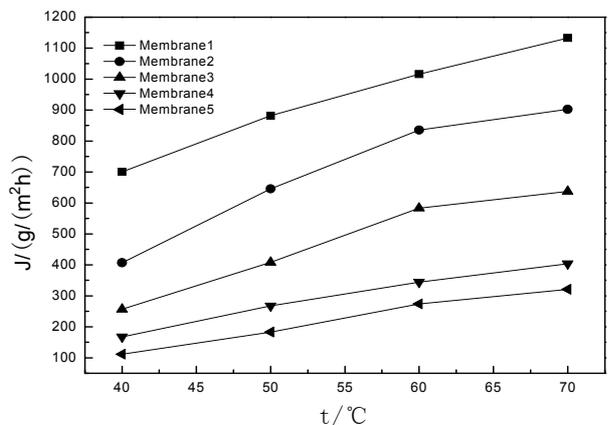


Figure 4. Comparison of different membrane permeation flux under different temperature

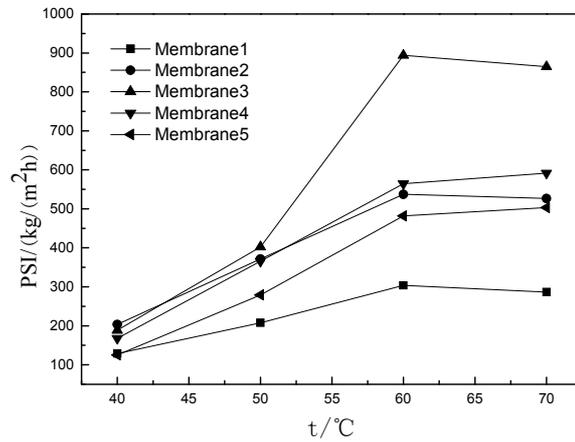


Figure 5. Comparison of different membrane PIS under different temperature

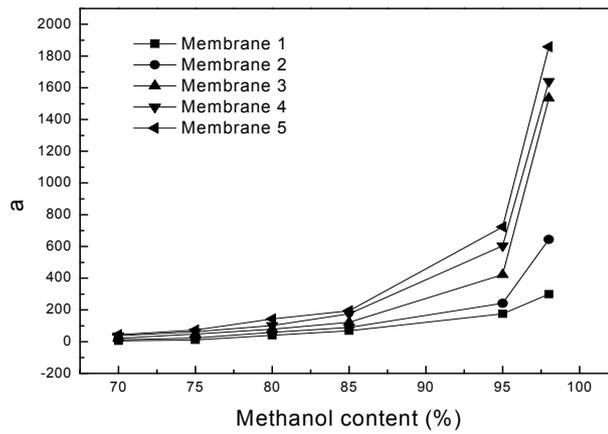


Figure 6. Effect of solution concentration on separation factor of different membrane

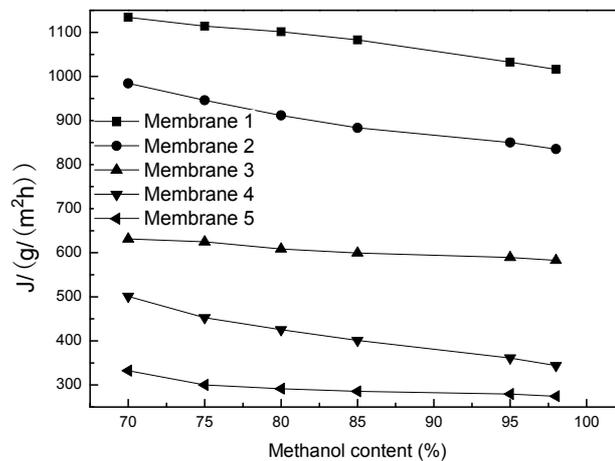


Figure 7. Effect of solution concentration on permeation flux of different membrane

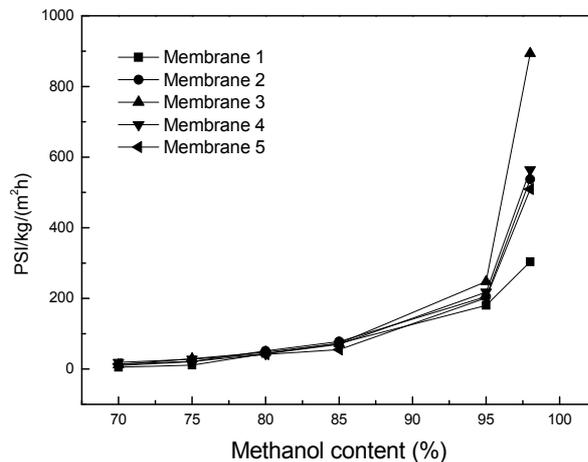


Figure 8. Effect of solution concentration on PIS of different membrane