

일반강연 II-4

## Pervaporation of Pyridine-Water Mixture through Poly(acrylonitrile-co-vinyl phosphonic acid) membrane

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## 폴리(아크리로나이트릴-비닐포스포닉산) 공중합체 막을 이용한 피리딘-물 혼합물의 투과증발분리

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### 1. Introduction

Among many azeotropic compounds, pyridine which forms an azeotropic mixture with three moles of water boiling at 92~93°C is very useful synthetic intermediate in laboratory and industry. With conventional separation method, the dehydration of pyridine aqueous solution is difficult and requires strong drying chemicals. To overcome these difficulties, several researchers have investigated on the separation of pyridine from aqueous solution through polymer membranes. Kujawski reported several ion-exchang membranes containing carboxylic and sulfonic functional group for dehydration of aqueous pyridine solution [1].

We have applied the idea of activation of water transport through ion-dipole interactions between polymer membrane and aqueous feed. Our previous studies reported on the *in-situ* complex membrane to separate water from aqueous pyridine solution based on simple acid-base theory [2,3]. Water transport was enhanced through *in-situ* complex formation between the acid moiety in the membrane and the incoming pyridine moiety in the feed. In this case, a catalytic mechanism was proposed. in the present study, we applied the same idea but changed the acid groups in the copolymer. We used phosphonic acid group in the copolymer membrane

In this presentation, we will report on the dehydration of aqueous pyridine

solution by using a poly(acrylonitrile-co-vinyl phosphonic acid) membrane and to compare the result with those for other membranes.

## 2. Experimental

The condition and designation of copolymerization are listed in Table 1. 250ml distilled water was placed in a four-necked-round flask under nitrogen atmosphere. After sufficient nitrogen purge, predetermined amounts of acrylonitrile and vinyl phosphonic acid monomers were poured into the flask. Then, potassium persulfate was added after heating the mixture up to 70°C. The copolymerization was carried out for 3 hours.

Synthetic copolymers were dissolved in dimethylformamide solution and poured into glass plate to be prepared with membranes. The thickness of the membranes was approximately 100  $\mu\text{m}$ .

## 3. Results and discussion

Fig. 1 illustrates the FT-IR spectra of virgin PANVP. As shown, the stretching peak of  $-\text{P}=\text{O}$  in vinyl phosphonic acid appears at  $\sim 990\text{cm}^{-1}$ , and the peak intensity of  $-\text{P}=\text{O}$  increased with increasing vinyl phosphonic acid content of PANVP copolymers.

Table 2 shows the molecular weight of PANVP copolymers measured by GPC. The standard materials of was polystyrene. PANVP copolymers have the number average molecular weight of 100,000~160,000 g/mole. Molecular weight of PANVP copolymers decreased with increasing vinyl phosphonic acid contents.

Pervaporation performances of PANVP3 membrane using 59wt% aqueous pyridine solution as a feed measured at 30°C~75°C are described in Fig. 2. In this figure, total flux of PANVP3 membrane depended on the operating temperature. The flux of PANVP3 membrane increased as operating temperature increased from 30°C to 75°C. Meanwhile, separation factor of PANVP3 membrane did not decrease with operating temperature. The reason for excellent dehydration capability of PANVP3 membrane can be explained by *in-situ* complex membrane concept as we previously suggested for dehydration of pyridine solutions. That is, because *in-situ* complex is formed between acid component in the membrane and pyridine from the feed, PANVP membrane interacts with water molecules in the feed and induced ion-dipole interaction, which promotes water transport from aqueous pyridine solution. Thermal motion of *in-situ* complex enhances the total flux of PANVP membranes at an elevated temperature.

Table 1. Designation of poly(acrylonitrile-co-vinyl phosphonic acid)

sample	acrylonitrile(wt%)	vinyl phosphonic acid(wt%)
PANVP1	99	1
PANVP2	95	5
PANVP3	90	10
PANVP4	85	15

water=250ml, potassium persulfate=0.5g

Table 2. Molecular weight of PANVP copolymers measured by GPC

sample	molecular weight( $\times 10^5$ )
PANVP1	1.6
PANVP2	1.3
PANVP3	1.1
PANVP4	1.0

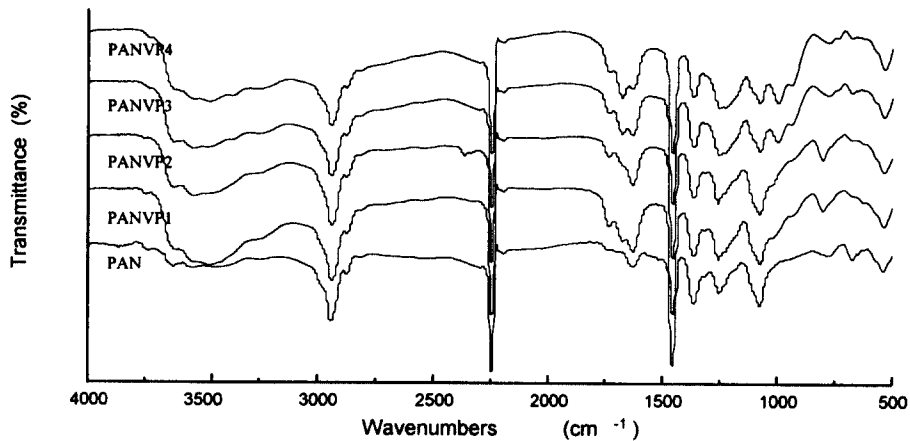
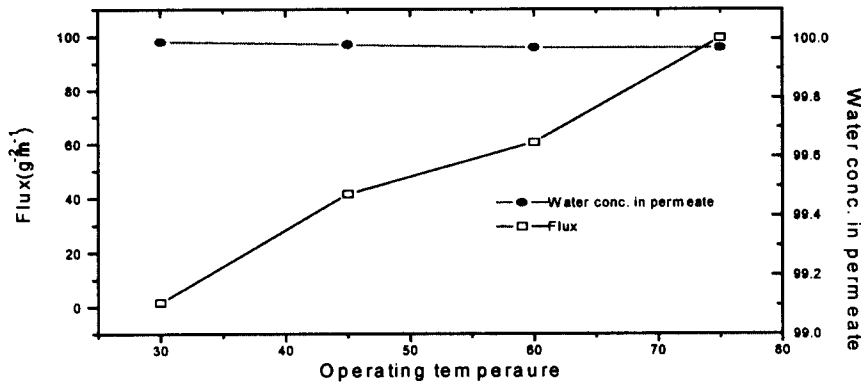


Fig. 1 FT-IR spectra of poly(acrylonitrile-co-vinyl phosphonic acid)

Fig. 2 Effect of operating temperature on pervaporation performance through PANVP3 membrane



#### 4. References

1. W. Kujawski, T. Q. Nguyen and J. Neel, Sep. Sci. Tech., 26(8) (1991) 1109.
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3. Y. M. Lee and B. K. Oh, J. Membrane. Sci., 98 (1995) 183.