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Comparisons of Reverse Osmosis and Pervaporation Membrane Processes. II. Experimental Interpretations.

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역삼투와 투과 증발막 공정의 비교. II. 실험적 해석

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Abstract : Reverse osmosis(RO) and pervaporation(PV) membrane separation processes were compared with each other experimentally for the system of water-ethanol mixtures by using nylon 4 blended membranes. The separation effciencies of PV were better than those of RO as expected in previous paper covering the theoretical comparisons of both processes, however the permeabilities data showed erractic results due to the membrane imperfections.

요 약 : 역삼투 및 투과 증발막 분리공정이 nylon 4 blended 막을 사용하여 물-에탄올 계에 대하여 실험적으로 비교되어졌다. 위 두 공정의 이론적 비교를 다루었던 전 논문과 마찬가지로 투과 증발 공정의 분리 효율이 역삼투 공정의 경우 보다 더 좋음을 알 수 있었다. 그러나 투과도 데이타는 막의 결함들로 인하여 엉뚱한 결과를 보였다.

1. Introduction

The comparisons of RO and PV membrane separation processes has not been extensively studied. The transport mechanism of both RO and PV could be considered as solution-diffusion mechanism. Therefore the selectivity of both separation processes should be similar. In the previous paper[1], we discussed theoretically the comparison of RO and PV separation processes using Paul and Ebra-Lima model[2,3]. It was concluded that in most cases the permeabilities and separation factors in PV were greater than those in RO. Kimura et al.[4] investigated the comparison of RO and PV separation processes for the separation of water-ethanol mixtures using n-hexyldimethylsilylated poly(1-trimethylsilyl-1-propyne) (PTMSP). The results of Kimura et al. [4] strongly supported our results from the theoretical comparison in the previous paper.

In this paper, RO and PV membrane processes are discussed by using nylon 4 - nylon 6, nylon 6 - PAA blended membranes in terms of separation factors(or rejections) and permeabilities.

2. Experimental

2. 1. Materials

Nylon 4 polymers were synthesized in our laboratory by the CO_2 - initiated polymerization of 2 - pyrrolidone by using potassium 2 - pyrrolidonate as the catalyst and the CO_2/KOH/18 - Crown - 6 ether catalyst system[5]. The intrinsic viscosity of nylon 4 used varied from 2.23 to 6.07. Nylon 6 with molecular weight 42,000 and poly(acrylic acid) with molecular weight 150,000 (in 25 wt.% aqueous solution) were obtained from Polysciences Inc. Fully hydrolyzed poly(vinyl alcohol) of 72 - 60 grade was obtained from Du Pont. The solvents used in the present study were of analytical grade.

2. 2. Blended membrane preparation

2. 2. 1. Nylon 6 - PAA membrane

A 10 wt.% nylon 6 in 90 % formic acid and 10 wt.% aqueous solution of PAA were mixed by varying each component composition to form a homogeneous solution. The film was cast onto a clean glass plate with a Gardner knife of predetermined drawdown thickness. Thus prepared film was then crosslinked in a 10 wt.% aluminum nitrate crosslinking bath for 30 hrs.[6], then immersed in deionized water for 24 hrs. with frequent water changes.

2. 2. 2. Nylon 4 - Nylon 6 membrane

An 8 wt.% nylon 4 solution and a 10 wt.% nylon 6 in 90 % formic acid were blended at various compositions to form a homegeneous solution. Then the membrane was prepared via the same procedures described above.

2. 3. Apparatus and experimental procedures

Reverse osmosis : A batch type cell with an effective membrane permeation area of 19.6cm^2 was used for RO. The feed solution was pressurized at 600 psia by nitrogen gas and stirred by a magnetic stirrer. The feed temperature was maintained at 25 ℃.

2. 3. 1. Pervaporation

Details of the permeation cell, the pervaporation apparatus and experimental procedure were described in ref.[7]. The required vacuum in the downstream side was maintained by a vented exhaust. The vacuum was measured by a Fisher, closed end, Bennet type vacuum manometer in the vacuum line near the cell and was always kept below 2 mmHg. The analysis of the permeate was performed by using a Anton - Paar DMA 60 digital densitometer[7].

3. Results and Discussion

The permeability obviously depends on the concentration gradient across the membrane front surface (v_{1o}) and membrabe back surface (v_{1l}), no matter what concentration difference is caused by applying a vacuum at the permeate side or by rasing the pressure at the feed side. Theoretically the permeate flux in PV is equal to that in RO whose applied pressure is infinite and the separation potential of PV is much higher than that of RO[1].

Figs. 1, 2 and 3 show the separation efficiencies of RO and PV for nylon 4 - nylon 6 and nylon 6 - PAA blended membranes in terms of separation factor ($\alpha_{w/o}$) and ethanol rejection. In most cases, the selectivies in PV are greater than those in RO. For nylon 4 - nylon 6 (6:4) blended membranes, when RO is compared to PV in terms of separation factor, the separation factor of PV at each feed composition is higher than that of RO. However the separation efficiency at 50 wt.% ethanol feed concentration is the highest in RO and is the lowest in PV. The nylon 4 - nylon 6 (8 : 2) blended membrane shows the similar trend in both separation processes. It was reported in the

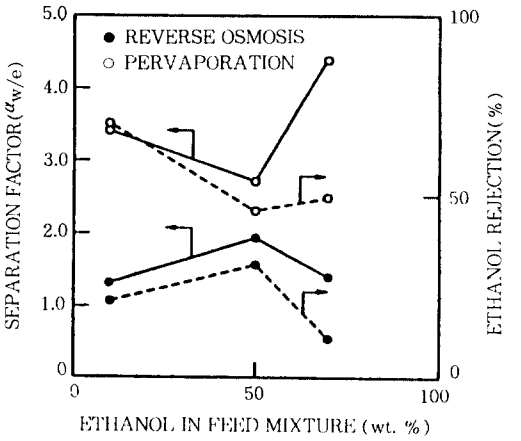

Fig. 1. Separation factor(or rejection) vs. ethanol concentration in feed for the nylon 4 - nylon 6 (6 : 4) blended membrane.

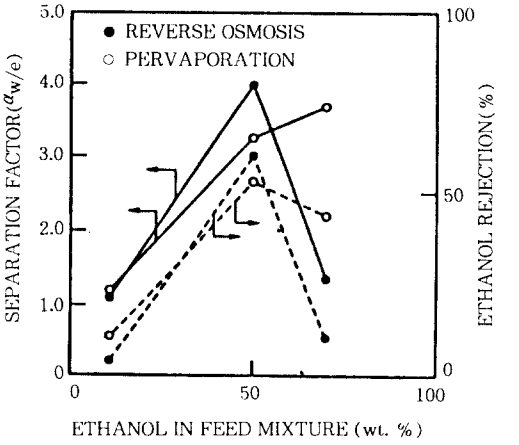

Fig. 2. Separation factor (or rejection) vs. ethanol concentration in feed for the nylon 4 - nylon 6 (8 : 2) blended membrane.

previous paper that the activities of certain component at the membrane back surface were theoretically dependent on the applied pressure in RO and the reduced pressure in PV. In this study, the activity of less preferential component, ethanol, at the membrane back surface in RO could be larger than that in PV. Therefore, the separation factors ($\alpha_{w/e}$) in PV are larger throughout the

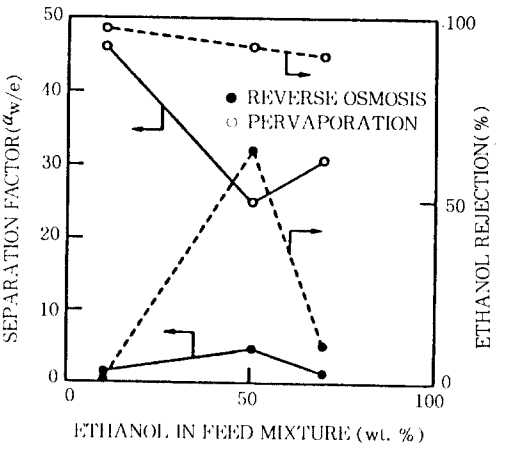

Fig. 3. Separation factor (or rejection) vs. ethanol concentration in feed for the nylon 6 - PAA (25 wt.%) blended membrane.

entire composition range. Another observation from these two kinds of membrane is that the separation efficiency at 50 wt.% ethanol feed concentration for nylon 4 - nylon 6 (6 : 4) membrane is lower than that for nylon 4 - nylon 6 (8 : 2) membrane, while the separation efficiencies at the other two feed concentrations for nylon 4 - nylon 6 (6 : 4) membrane are higher. In general, the gradual addition of more hydrophilic polymer allows the more swelling for water, as a result, the other component (ethanol) can permeate very easily in the presence of water. This could explain the reason of above phenomena. For nylon 6 - PAA blended membranes, the membrane selectivity in PV is much higher than that in RO.

Figs. 4, 5 and 6 show the permeabilities of RO and PV. It was expected that the permeabilities of PV membranes were larger than those of RO membranes as explained in the previous paper dealing with the theoretical comparison of RO and PV since the concentration gradient in PV is larger. However, experimental results showed the discrepancy with the theoretical expectations, which could be caused by the membrane imperfections. It has been reported that the membrane imperfections

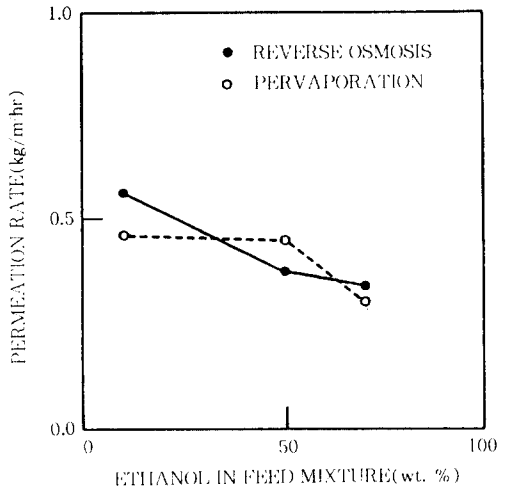

Fig. 4. Permeation rate vs. ethanol concentration in feed for the nylon 4-nylon 6 (6 : 4) blended membrane.

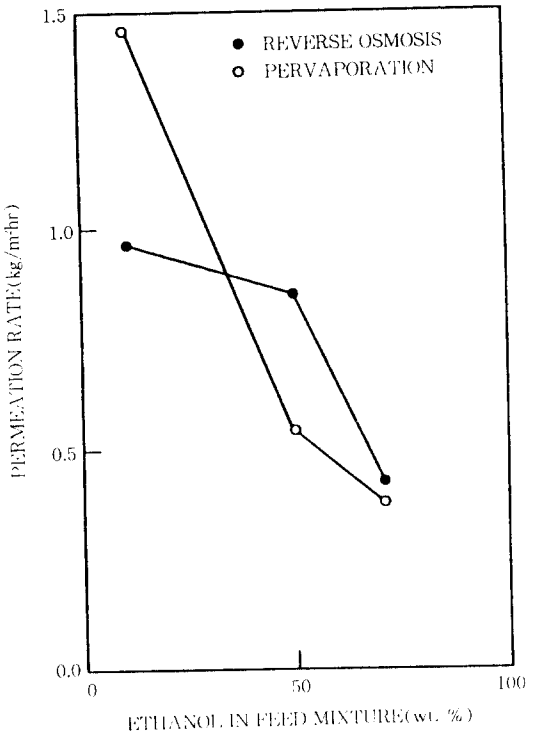

Fig. 5. Permeation rate vs. ethanol concentration in feed for the nylon 4-nylon 6 (8 : 2) blended membrane.

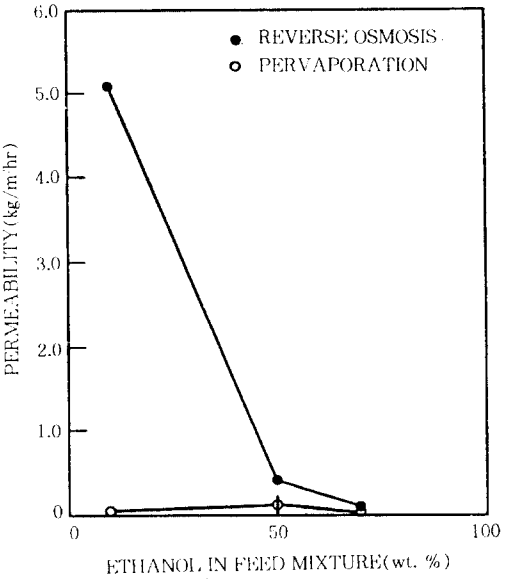

Fig. 6. Permeation rate vs. ethanol concentration in feed for the nylon 6-PAA (25 wt.%) blended membrane.

affect the selectivity and flux in RO process, while does not have any influence on selectivity and flux in PV process[8]. Therefore, reducing the imperfections through the membrane annealing at high temperatures in RO may allow to approach the same selectivity and flux as in PV.

4. Conclusions

RO and PV membrane separation efficiencies are experimentally compared with each other for the system of water-ethanol mixtures by using nylon 4 blended membranes. As expected in the previous paper dealing with the theoretical comparison of RO and PV membrane separation processes, the separation efficiencies of PV are much better than those of RO in most feed concentration of ethanol. However, the permeabilities show erractic results due to the membrane imperfections. According to the previous paper, the permeabilities in PV are also higher than those in RO, however the flux in RO at

certain ethanol feed concentration are noticed larger than flux in PV. Therefore, membrane annealing process before experiments, in general, would be needed to get the same permeability and separation efficiency in both processes.

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