

Pervaporation Separation of Water from Aqueous TFEA Solution by NaY Zeolite Membrane

Hyunsoo Jeon, Hyoseong Ahn, Youngjin Lee, Inho Song, Hyeryeon Lee, Yongtaek Lee[†], In Jun Park*, and Soo-Bok Lee*

Department of Chemical Engineering, Chungnam National University, 220 Gung-dong, Yuseong-gu, Daejeon, 305-764, Korea

*Advanced Chemical Technology Division, Korea Research Institute of Chemical Technology

P.O. Box 107, Yuseong-gu, Daejeon, 305-600, Korea

(Received October 17, 2006, Accepted December 5, 2006)

Abstract: Pervaporation of water/2,2,2-trifluoroethanol (TFEA) mixtures was performed using a NaY zeolite membrane which was prepared by a hydrothermal synthesis. Pervaporation with a zeolite membrane is one of the economic separation technologies for liquid mixtures including organic/water solutions. The effects of a TFEA feed concentration and a temperature were studied on the permeation flux and the separation factor. Not only the water flux increased significantly with the increase of the operating temperature, but also the TFEA flux through the NaY zeolite membrane rapidly increased with the increase of the temperature at the feed concentration below 0.8 mole fraction of TFEA.

Keywords: *pervaporation, zeolite membrane, NaY, TFEA aqueous solution, separation*

1. Introduction

The chemical separation by a pervaporation technique is one of the interesting areas of the current membrane research[1]. Pervaporation is a combination process of a preferential permeation followed by an evaporation. Pervaporation might have a great potential for application in various separation processes since it is not only an economic separation technology but also an environmentally clean technology[2,3]. On one side of the membrane the feed solution is in the liquid state, and it is withdrawn through the membrane as a preferentially sorbed vapor by applying a vacuum on the other side of the membrane[4].

The possible application areas for pervaporation separation in industry are numerous, including separation of azeotropic mixtures[5,6], separation of mixtures of

organic liquids[7,8], dehydration of organic solvents [9,10] and continuous removal of one of the products of reaction from a bioreactor[11]. Separation of the liquids is governed by the chemical nature of the permeating species as well as that of the membrane material, and the morphology of the membrane itself together with the experimental conditions of process operation[12,13].

Purification of organic solvents such as TFEA (2,2,2-trifluoroethyl alcohol), containing a small amount of water is of vital significance in the area of the organic synthesis. TFEA has been used as one of the chemicals for anesthetics and sedatives. It is also used as an intermediate for the organic synthesis, a solvent, optical and electronic functional materials, fluorine containing esters and a base material for copolymers including fluorine. Especially, 3FMA (2,2,2-trifluoroethyl methacrylate) is a very useful ester for applications of contact lenses and paints since it shows not only a low re-

[†]Author for all correspondences
(e-mail : ytleec@cnu.ac.kr)

Table 1. Physical Properties of TFEA

Chemical structure	CF ₃ CH ₂ OH
Molecular weight	100.04
Boiling Point (°C)	73.6
Melting Point (°C)	-43.5
Specific Density	1.3842
Refractive Index (n _D ²⁰)	1.2907
Dipole Moment (Debye)	2.04
Heat of Vaporization (kJ/mol)	35.15
Viscosity (cp at 20 °C)	0.9

fractive index and a high waterproof function but also easy ability of copolymerization with acrylate or methacrylate[14]. During the synthesis of 3FMA, water is produced as a byproduct of the esterification process. An economic manufacturing process for 3FMA could be designed if an efficient water removal process is applied. Table 1 shows physical properties of TFEA.

In this study, NaY type zeolite membranes were prepared on the inner surface of α -porous alumina support tube by a hydrothermal process. The synthesized NaY zeolite membrane was used as a water selective membrane to separate water from an aqueous feed solution containing TFEA. The separation characteristics were investigated and compared through the NaY zeolite membrane.

2. Experimental

2.1. Preparation and Analysis of Membrane

NaY zeolite membranes were synthesized from liquid mixtures in which the chemical compositions were 10 SiO₂ : 1 Al₂O₃ : 14 Na₂O : 840 H₂O. Sodium silicate solution (Samchun, Korea) was used as a source material for Si; sodium aluminate (Wako, Japan) and sodium hydroxide (Daejung, Korea) were used as source chemicals for Al and Na, respectively. After preparing a Si solution and an Al solution, the Si solution was added to the Al solution and mixed for 4 hours to get the aging gel. Both ends of the support tube (α -alumina tube, USF/Schmacher, O.D. 10 mm,

I.D. 7 mm, length 47 mm, mean pore size 0.2 μ m, porosity 0.33) were glazed to be used as the sealed area for O-ring. Molecular sieve NaY (mean particle size: $\leq 5 \mu$ m, Aldrich, U.S.A.) powders were used as seed crystals. They were rubbed on the inside surface of a support with a sponge brush. The seeded support and an autoclave were preheated at 40°C for 1 hour. The mixed solution was carefully poured in the inside of the support. Then, the support was wrapped with teflon tapes to prevent not only growing crystals on the outside of the support but also leaking out of solution. After that, the wrapped support was placed vertically in the autoclave. NaY zeolite membranes were synthesized under the reaction temperature of 90°C and the reaction time of 12 hours. The synthesized zeolite membranes were washed with distilled water and dried at 100°C for 8 hours.

The crystal structure of the zeolite membrane was confirmed with a XRD (D/Max-2200 Ultima/PC, Rigaku Co., Japan, 30 kV, 15 mA) and the morphology was analyzed with a SEM (JSM-6300, Jeol Ltd., Japan).

2.2. Pervaporation

The separation experiments were carried out using a pervaporation apparatus as schematically shown in Fig. 1. The zeolite membrane was sealed with two viton O-rings (I.D. 9 mm) in both sides; the membrane was installed in the membrane test cell. The aqueous TFEA solution was fed and circulated with a metering diaphragm pump (DMA-05, Daekyung, Korea). The TFEA concentration was maintained between 0.6 and 0.95 mole fraction. The permeate was collected in a liquid N₂ trap in which the pressure was maintained under 5 mmHg. The experiments were performed in the temperature range of 25~60°C. Both the feed and the permeate concentrations were analyzed with a gas chromatograph (M600D, Younglin Co., Korea) in which a Porapak Q (Supelco, U.S.A.) column and a FID (flame ionization detector) were equipped.

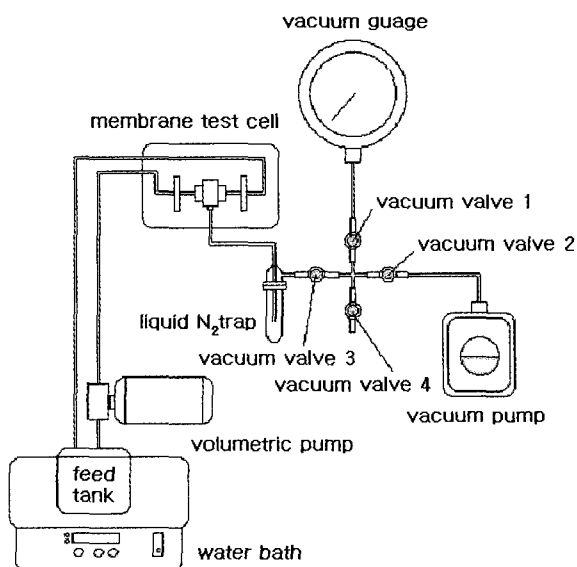


Fig. 1. A schematic diagram of pervaporation apparatus.

2.3. Pervaporation Characteristics

Pervaporation characteristics could be presented in terms of a flux and a separation factor which are defined as follows:

$$\text{Flux} = \frac{P}{A \cdot t}, \quad \text{Separation factor} = \frac{y_{H_2O} / y_{TFEA}}{x_{H_2O} / x_{TFEA}}$$

where P represents a weight of the permeate (g), A denotes the membrane area (m^2), t is the permeation time (hr), y_{H_2O} and y_{TFEA} refer to mole fractions of water and TFEA at the permeate side, respectively. x_{H_2O} and x_{TFEA} represent mole fractions of water and TFEA in a feed solution, respectively.

3. Results and Discussion

3.1. Characterization of Membrane

Fig. 2 shows XRD pattern of the synthesized NaY zeolite membrane together with the pattern of reference standard zeolite.

The synthesized NaY zeolite showed nearly the same XRD pattern as that of NaY (molecular sieve NaY, Aldrich, U.S.A.) zeolite.

SEM images of the synthesized NaY zeolite mem-

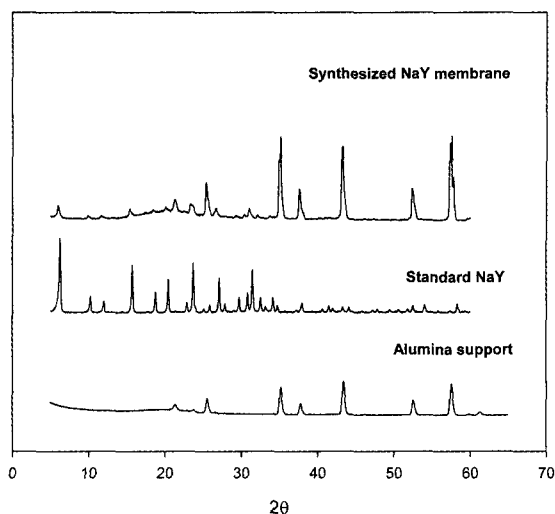


Fig. 2. XRD pattern of NaY zeolite membrane.

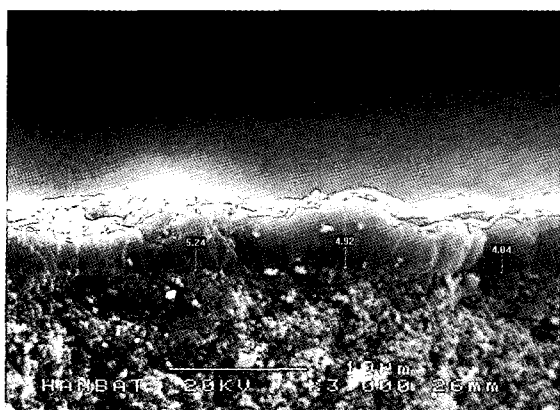
brane were shown in Fig. 3. As shown in Fig. 3, the synthesized NaY zeolite crystals were randomly grown to the size of $1\sim 2 \mu m$ with a zeolite layer thickness of about $5 \mu m$.

3.2. Water Flux

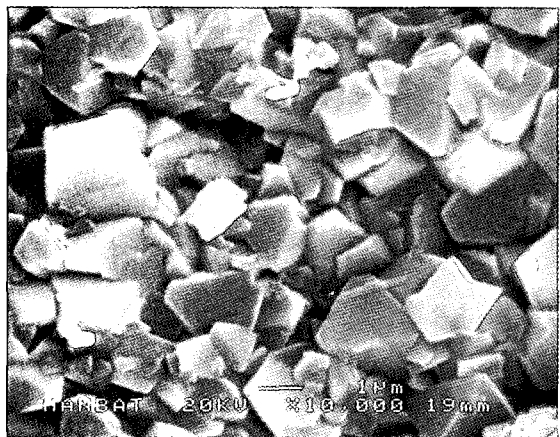
Water fluxes through NaY zeolite membrane are shown in Fig. 4. The water flux decreased as the mole fraction of TFEA in the feed solution increased. Additionally, the water flux increased as the temperature increased for NaY zeolite membrane. This may be due to the change of the fugacity of water which is a driving force of the pervaporation as denoted in the literature [15]. The water fluxes through the NaY zeolite membrane were between $682 \text{ g/m}^2/\text{h}$ and $8000 \text{ g/m}^2/\text{h}$.

3.3. TFEA Flux

Fluxes of TFEA compounds through the NaY zeolite membrane are shown in Fig. 5. The TFEA fluxes increased as both the mole fraction of TFEA and the temperature increased. This may be due to the increment of the partial vapor pressure of organic compounds. The increment of either the concentration or the temperature results in the increment of a partial vapor pressure, leading to the increase of TFEA flux. TFEA fluxes increased from 2.1 to $225 \text{ g/m}^2/\text{h}$ within



(a) a cross-sectional view



(b) a top view

Fig. 3. SEM images of the NaY zeolite membrane. (a) a cross-sectional view, (b) a top view.

the feed concentration of 0.65~0.95 mole fraction of TFEA and the temperature of 25~60°C.

3.4. Separation Factor

Fig. 6 shows the separation factors of water through the NaY zeolite membrane. The separation factor decreased as the mole fraction of TFEA increased and a temperature. The increasing rate of a TFEA flux is larger than that of a water flux, resulting in the decrease of the separation factor. This change behavior was observed in the entire range of mole fraction of TFEA. The separation factors of water were observed to be from 736 to 7000 within the feed concentration of 0.65~0.95 mole fraction of TFEA and the temperature of 25~60°C. The NaY zeolite membrane might be good enough to separate water from TFEA/water

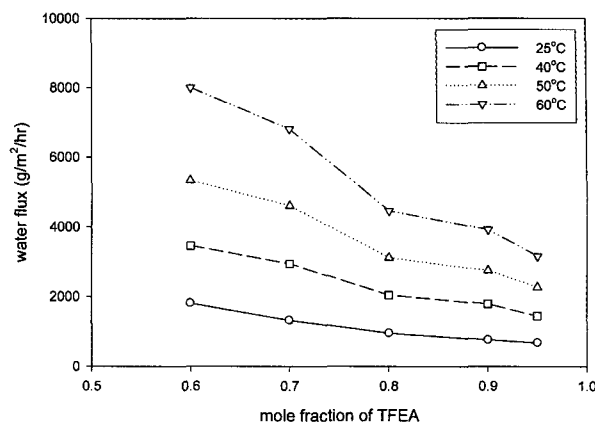


Fig. 4. Water fluxes through NaY zeolite membrane.

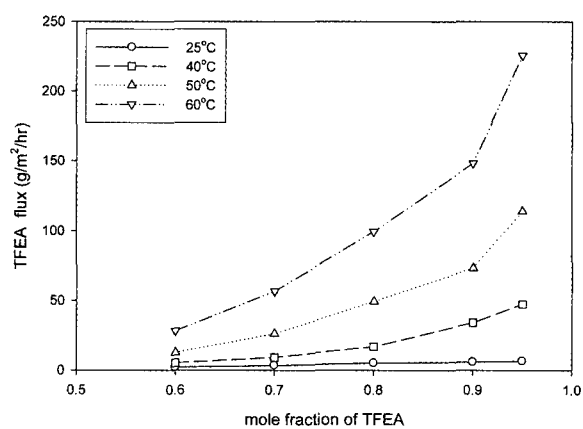


Fig. 5. TFEA fluxes through NaY zeolite membrane.

mixture at this typical concentration of TFEA in the feed solution.

4. Conclusions

NaY zeolite membrane was successfully synthesized on the inner surface of a porous α -alumina supports and it was shown that water could be excellently separated from TFEA/water mixtures by the pervaporation using the NaY zeolite membrane. The flux and the separation factor through NaY zeolite membranes were strongly affected by both the feed concentration and the operating temperature. Finally, the NaY zeolite membrane might be used as a hydrophilic pervaporation membrane to separate water from the aqueous TFEA solution.

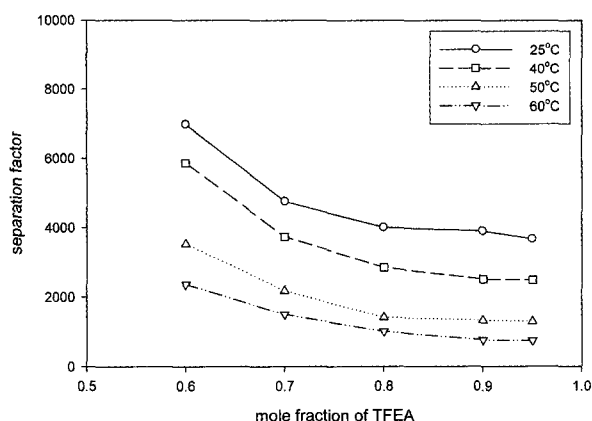


Fig. 6. Separation factors of water through NaY zeolite membrane.

Acknowledgement

This research was supported by a grant (CD2-102) from Carbon Dioxide Reduction & Sequestration Research Center, one of the 21st Century Frontier Programs funded by the Ministry of Science and Technology of Korean Government.

References

1. T. Uragami, K. Okazaki, H. Matsugi, and T. Miyata, Structure and permeation characteristics of an aqueous ethanol solution of organicinorganic hybrid membranes composed of poly(vinyl alcohol) and tetraethoxysilane, *Macromolecules*, **35**, 9156 (2002).
2. C. C. Pereira, A. C. Habert, R. Nobrega, and C. P. Borges, New insights in the removal of diluted volatile organic compounds from dilute aqueous solution by pervaporation process, *J. Membr. Sci.*, **138**, 227 (1998).
3. D. Hofmann, L. Fritz, and D. Paul, Molecular modeling of pervaporation separation of binary mixtures with polymeric membranes, *J. Membr. Sci.*, **144**, 145 (1998).
4. V. A. Tuan, S. Li, J. L. Falconer, and R. D. Noble, Separating organics from water by pervaporation with isomorphously-substituted MFI zeolite membranes, *J. Membr. Sci.*, **196**, 111 (2002).
5. J. Neel, Introduction to pervaporation, in: R.Y.M. Huang (Ed.), Pervaporation membrane separation processes, Elsevier, Amsterdam, The Netherlands, 1 (1994).
6. A. A. Kittur, M. Y. Kariduraganavar, U. S. Toti, K. Ramesh, and T. M. Aminabhavi, Pervaporation separation of waterisopropanol mixtures using ZSM-5 zeolite incorporated poly(vinyl alcohol) membranes, *J. Appl. Polym. Sci.*, **90**, 2441 (2003).
7. D. Sarkhel, D. Roy, M. Bandyopadhyay, and P. Bhattacharya, Studies on separation characteristics and pseudo-equilibrium relationship in pervaporation of benzenecyclohexane mixtures through composite PVA membranes on PAN supports, *Sep. Purif. Technol.*, **30**, 89 (2003).
8. S. C. George, K. N. Ninan, and S. Thomas, Pervaporation separation of chlorinated hydrocarbon and acetone mixtures with crosslinked styrene-butadiene rubber and natural rubber blend membranes, *J. Membr. Sci.*, **176**, 131 (2000).
9. S. P. Kusumcahyo and M. Sudoh, Dehydration of acetic acid by pervaporation with charged membranes, *J. Membr. Sci.*, **161**, 77 (1999).
10. M. Y. Kariduraganavar, S. S. Kulkarni, and A. A. Kittur, Pervaporation separation of wateracetic acid mixtures through poly(vinyl alcohol)silicone based hybrid membranes, *J. Membr. Sci.*, in press.
11. X. Lin, E. Kikuchi, and M. Matsukata, Preparation of mordenite membranes on α -alumina tubular supports for pervaporation of waterisopropyl alcohol mixtures, *Chem. Commun.*, 957 (2000).
12. R. Y. M. Haung, R. Pal, and G. Y. Moon, Cross-linked chitosan composite membrane for the pervaporation dehydration of alcohol mixtures and enhancement of structural stability of chitosan/poly-sulfone composite membranes, *J. Membr. Sci.*, **160**, 17 (1999).
13. X. Feng and R. Y. M. Haung, Liquid separation by membrane pervaporation: a review, *Ind. Eng. Chem. Res.*, **36**, 1048 (1997).
14. F-TECH Incompany Catalog, F-TECH, Inc. (2001).
15. T. C. Bowen, S. Li, R. D. Noble, and J. L. Falconer, Driving force for pervaporation through zeolite membranes, *J. Membr. Sci.*, **225** 165 (2003).