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Mixed-matrix membrane prepared from crosslinked PVA with NaA zeolite for pervaporative separation of water–butanol mixtures

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ABSTRACT

The NaA zeolite particles are dispersed in a poly(vinyl alcohol)(PVA) matrix to prepare a mixed-matrix membrane (MMM). Pervaporation characteristics such as a permeation flux and a separation factor are investigated in terms of the feed concentration of *n*-butanol together with a variety of the wt.% of NaA zeolite particles in the membrane. The nano sized zeolite particle of NaA was found to be 63.5 nm. Also, micro sized particle was less than 5 μm. The *n*-butanol concentration was changed from 0.01 to 0.05 mol fraction with an interval of 0.01 mol fraction, while the pressure of permeation side was about 3 mmHg. The wt.% of the NaA zeolite particles varied between 0 wt.% and 5 wt.%. The effect of the NaA zeolite particles was observed that the flux of water through the MMM was a factor of 2.5 increased compared to the pure PVA membrane at the typical operation condition. When the nanosized of particles was dispersed in the MMM instead of the microsized particles, the flux of water was approximately 20% increased, compared to that through the MMM containing the microsized NaA particles. In addition, the separation factor of water was 5% increased.

Keywords: Pervaporation; *n*-butanol; MMM; NaA zeolite

1. Introduction

For a membrane separation, the solubility and the diffusivity of each component of the mixture in a membrane are the key parameters for the separation performance. To achieve a satisfactory separation performance, the membrane should preferentially absorb and facilitate the transport of the separated species [1]. Pervaporation is a membrane-based separation technique giving a potential application in dehydration of liquid mixtures [2]. Unlike the conventional distillation where the separation depends on the vapor–liquid equilibrium, the pervaporation separates the liquid mixtures by the difference in the

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affinity with a membrane and the diffusivity of each liquid component in a membrane [3].

One of the key successes of the pervaporation is that, if suitable membranes can be fabricated with high permeability and good selectivity to water, it is possible to achieve an excellent separation [4]. However, a number of novel polymeric membranes are needed for a successful operation of the process in view of the fact that the pervaporation is environmentally cleaner than a conventional distillation.

One expects a membrane with high pervaporation performances in flux and selectivity, good membrane forming properties, as well as high mechanical properties. The membrane mechanical properties are of importance for successful membrane separation technologies. The pervaporation is not only an economical separation technology since it needs an electric power to maintain the permeate side in vacuum but is also an environmentally clean technology in which potential pollution sources such as entrainers for azeotropic distillation are not needed [5].

The pervaporative separation mechanism is known to be the sorption-diffusion: firstly, a sorption into the membrane has to occur at the upstream side, secondly, a diffusion through the membrane, and thirdly, a desorption into the vapor phase at the downstream side [6].

A hydrophilic membrane might be used to separate water from water/organic mixtures. Even if hydrophilic polymeric membranes showed a high selectivity, they were known to be very sensitive to the operational condition such as the feed concentration and the temperature. A mixed-matrix membrane might be useful for water pervaporation since it shows not only molecular sieve effects but also good thermal, chemical, and mechanical stabilities [7].

Gao et al. [8] have fabricated hydrophilic composite membranes consisting of microsized NaA zeolites and poly(vinyl alcohol)(PVA) for the pervaporation of ethanol/water pervaporation. They observed that the flux of 172 ml/m^2/h and separation factor of 36.6 at 50°C.

Adoor et al. [9] have reported the use of the mixed-matrix membrane (MMM) of PVA containing sodium montmorillonite clay for pervaporation of water–isopropanol mixtures. Their MMM showed a water flux range between 151 g/m^2/h and 184 g/m^2/h at 10 wt.% of water in a feed solution and the temperature range of 40–50°C. On the other hand, the separation factors were in the range of 217–1,314.

Khayet et al. [10] have reported the use of poly (2,6-dimethyl-1,4-phenylene oxide) membranes filled with silica and silane nanosized particles for methanol/water mixtures pervaporation. They observed that the total fluxes ranged between 50 g/m^2/h and 200 g/m^2/h at 0 wt.%-100 wt.% of methanol concentration in their feed aqueous solution. In addition, the methanol fluxes ranged from 0 g/m^2/h to 200 g/m^2/h.

Guan et al. [11] have developed the multilayer MMM consisting of the KA zeolite 3A-filled PVA selective layer, the porous poly(acrylonitrile-co-methyl acrylate) intermediate layer and the polyphenylene sulfide non-*woven* fabrics substrate for the dehydration of ethanol/water mixture. Their membrane showed an ethanol flux between 0.03 g/m^2/h/kPa and 14 g/m^2/h/kPa with 0 wt.%-30 wt.% of KA zeolite content in the membrane at 20 wt.% of ethanol concentration in a feed aqueous solution.

Okumus et al. [12] have shown that the addition of zeolite particles to cellulose acetate matrix caused a decrease in selectivity owing to the microporous cave-like structures and an increase in flux owing to the increased porosity.

In this study, the pervaporative dehydration of water–*n*-butanol mixtures was experimentally carried out using the MMM prepared from crosslinked PVA with NaA zeolite particles. The nanosized NaA zeolite particles might have many advantages over the microsized NaA zeolite particles, since not only they provide larger surface area, but also a thin MMM can be fabricated. Since, there are few reports on the comparison of the separation performance of the MMMs where either the nanosized NaA zeolite particles or the microsized NaA zeolite particles are dispersed, both the MMMs were used to remove water by pervaporation and the experimental results were compared.

2. Experimental

2.1. Materials

PVA (code: 341584, Sigma Aldrich) with a 99% degree of hydrolysis was used as a dense membrane material and ethylene glycol diglycidyl ether (EGDE, EP grade, Sigma Aldrich) with a content of 50 wt.% as a crosslinking agent. The following chemicals were utilized to synthesize the nanosized NaA particles and all chemicals were supplied by Sigma Aldrich: sodium hydroxide (1.0 N) as a Na source, aluminum isopropoxide with a content of 98 wt.% as an Al source, Ludox HS 30 with a content of 30 wt.% silica as a silica source and tetra methyl ammonium hydroxide (TMAOH, 25 wt.% in H_2O). Commercially available NaA zeolite (Code: 233668, Molecular sieves, 4 Å, powder, <5 μm) was purchased from Sigma Aldrich. Water (HPLC grade) and n-butyl alcohol (GC grade, 99.5%) were purchased from Samchun, Korea.

2.2. Synthesis of the NaA zeolite particles

In Fig. 1, the synthesis procedure of the nanosized NaA zeolite particles is shown. The NaA zeolite particles were synthesized from a liquid solution in which the chemical compositions were $0.3Na_2O:11.25SiO_2:1.8Al_2O_3:13.4(TMA)_2O:700H_2O$. The first solution (I) was prepared by mixing Ludox HS 30 (2.25 g) and H_2O (2.0 g) following the adjustment of pH to 10. The second solution (II) was prepared by mixing aluminum isopropoxide (0.75 g), $TMAOH{\cdot}5H_2O$ (5.0 g), sodium hydroxide (0.6 g), and H_2O (7.0 g). After adding the solution (II) to the solution (I), its mixed solution was stirred for 24 h at the room temperature for the purpose of creating nuclei as many as possible. And then, the prepared solution was stirred in a silicon oil of 80°C further for 24 h to synthesize the nanosized NaA zeolite particles. The particles finally formed were collected by centrifugation (UNION55R, Hanil Co., Ltd) for 90 min at 10,000 rpm. Those particles were washed in water for 1 h together with ultra-sonication (3210R-DTH, Bransonic Co., Ltd). The washing procedure was repeated three times to completely clean the surfaces of the nanosized NaA zeolite particles. The crystal structure of the synthesized zeolite particles was confimed with a thin-film X-ray diffraction (XRD, D8 DISCOVER, B RUKER AXS Co., Germany, 30 kW). The size distribution of the synthesized NaA particles was measured using a Zeta-potential Analyzer (ELS-Z2, Otsuka Co., Korea).

2.3. Preparation of MMM dispersed with NaA zeolite

Fig. 2 shows the preparation procedure of the mixed-matrix membrane. Two different particle sizes of NaA zeolite were chosen: one is the nanosized NaA zeolite particles synthesized in our laboratory and the other one is the microsized NaA zeolite particles commercially available. The zeolite particles were dispersed in a 10.0 wt.% PVA aqueous solution under vigorous stirring for 24 h. The content of NaA particles in the MMM was controlled to be in the range from 1 to 5 wt.%, regardless of the size of NaA zeolite particles. EGDE was added to the PVA aqueous solution in which the NaA zeolite particles were suspended. After rigorous stirring for 24 h, the prepared solution was sonicated for 1 h and immediately casted on the Teflon plate to form a thickness of 100 µm using a doctor blade (Film applicator, Yoshimitsu, JP/YBA-3, 12.5–250 µm). The casted solution on the Teflon plate was evaporated to remove water at 40°C in a vacuum oven (17-VDO-25, Kukje Scien Co., Ltd) for 24 h, and then the thin film was completely crosslinked at 110°C for 1 h. The surface morphology of the casted MMM was measured by the scanning electron microscopy (SEM, JSM-7000-F, Jeol Ltd., Japan).

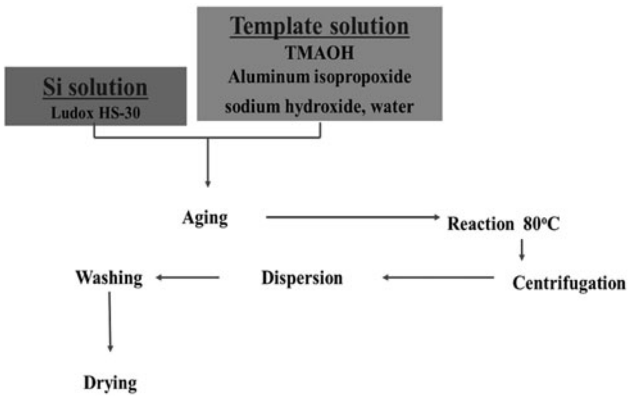


Fig. 1. Schematic synthesis procedure of nano sized NaA zeolite particles.

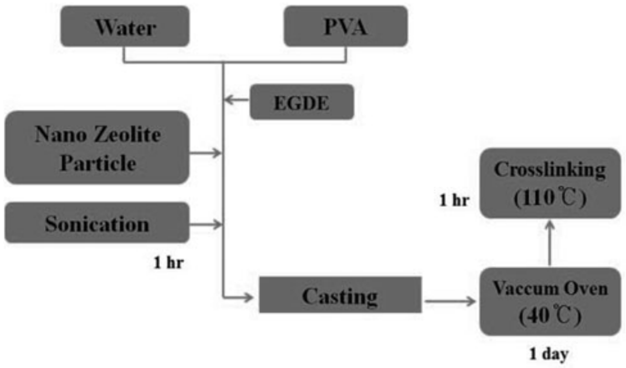
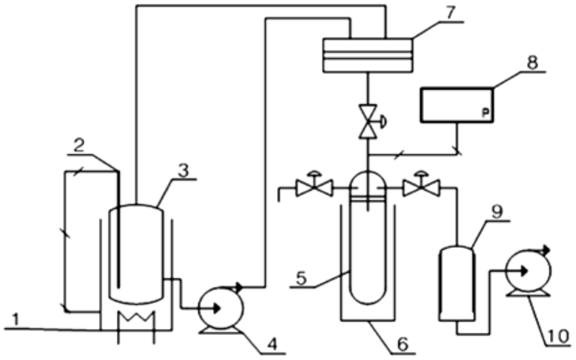


Fig. 2. Preparation of MMM dispersed with nano-sized NaA zeolite particles.

2.4. Pervaporation experiment

The pervaporation experiments were carried out using a pervaporation apparatus designed and set up as schematically shown in Fig. 3. The MMM was mounted in a stainless steel permeation cell in which the effective membrane area in contact with a feed solution was 11.93 cm^2. The aqueous feed solution was fed with a flow rate of 300 ml/min at 25°C and circulated with a diaphragm pump (DMA-05, Daekyung, Korea). The *n*-butanol concentration in a feed solution varied from 0.01 to 0.05 mol fraction. The permeate side of the membrane was maintained in a vacuum condition at 3 mmHg. The permeate was collected in a liquid nitrogen cold trap for a regulated time after a steady state was achieved in the pervaporation experimental system. In general, it took 3 h to arrive at the steady state.



(1) Thermostat; (2)thermocouple; (3)feed tank; (4)volumetric pump; (5)cold trap; (6)liquid nitrogen; (7)membrane cell; (8)pressure gauge; (9)desiccators; (10)vaccum pump.

Fig. 3. A schematic of pervaporation apparatus.

The concentrations of *n*-butanol in both the feed and the permeate were analyzed with a gas chromatograph (M600D, Younglin Co., Korea) where Porapak Q (Hewlett Packard, USA) column was equipped. A flame ionization detector (FID) was used to determine the concentration of *n*-butanol.

3. Results and discussion

3.1. Analysis of nanosized NaA zeolite particles and MMM

Fig. 4 shows that the XRD pattern of the synthesized NaA particles was compared to the standard NaA zeolite crystals. It was confirmed that the synthesized particles were known to be the NaA zeolite since the XRD pattern was the same as that of the standard NaA zeolite.

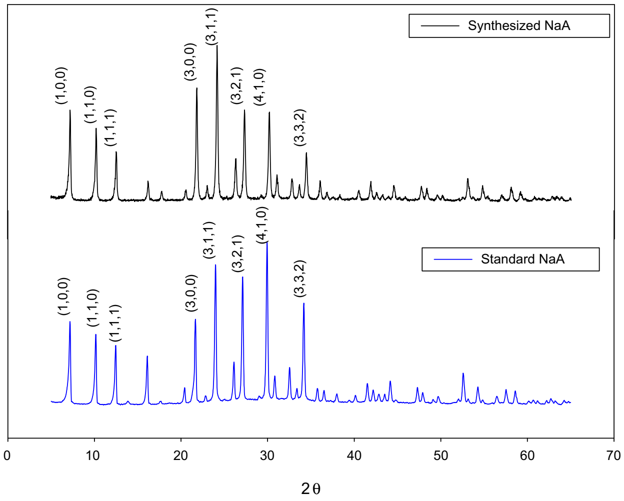


Fig. 4. XRD plots of synthesized NaA zeolite and standard NaA zeolite.

Fig. 5 shows the particle size distribution of the synthesized NaA zeolite particles. It is shown that the size of the synthesized NaA zeolite particles is ranged from 50 to 80 nm in diameter. It is observed that the mean diameter of the particles is 63.5 nm. It is thought that this particle size is small enough to fabricate the MMM as a thin film since the thickness of the membrane active layer would be in the range of few micrometers.

Fig. 6 shows the typical SEM images of surfaces of MMMs prepared with nanosized NaA zeolite particles of two different weight percent: (a) 1 wt.% and (b) 3 wt.%. As increasing the weight percent of NaA zeolite particles in the MMM, it is observed that the number of zeolite particles on the surfaces increases significantly. It is thought that the nanosized zeolite particles are partly agglomerated with each other, resulting in their dispersion on the surface as shown in Fig. 6.

3.2. *Performance of pervaporative separation*

Performance of pervaporative separation might be presented in terms of a flux and a separation factor defined as follows:

$$\text{Flux} = W/(A \times t) \quad (1)$$

$$\text{Separation factor} = (y_w/y_b)/(x_w/x_b) \quad (2)$$

where *W* represents the weight of permeate (g) collected in a cold trap, *A* is the effective membrane area (m^2), t is the permeation time (h); y_w and y_b refer to the mole fractions of water and *n*-butanol at the permeate side, respectively; x_w and x_b represent the mole fractions of water and *n*-butanol at the feed side, respectively.

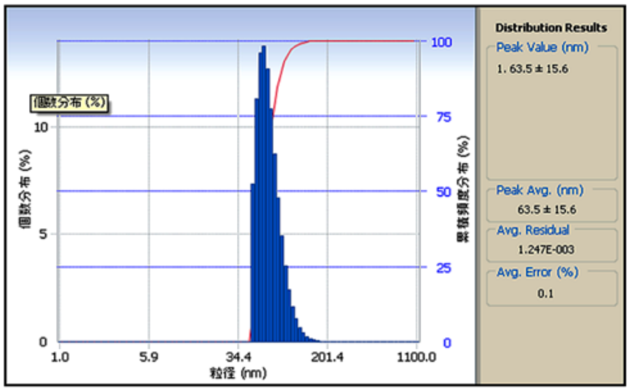


Fig. 5. Size distribution of synthesized NaA particles.

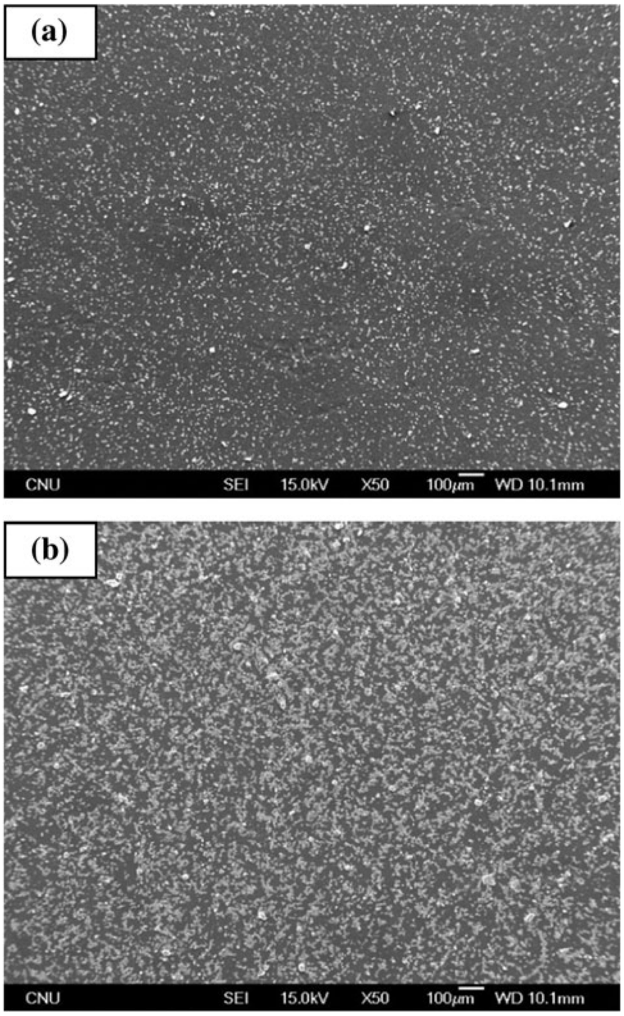


Fig. 6. SEM images of surfaces of MMMs prepared with nano sized NaA zeolite particles of different weight percent: (a) 1 wt.% and (b) 3 wt.%.

To understand the permeation behavior of water through the MMM for pervaporation, the flux of water is shown in Fig. 7. It can be seen that the water flux significantly decreases as the mole fraction of *n*-butanol increases no matter what the weight percent of zeolite is. When the zeolite particles are added to the pure PVA matrix to form the MMM, the water flux is observed obviously to increase. Also if the microsized NaA particles are replaced with the nanosized NaA particles, the water flux is shown to be slightly increased.

As can be seen in Fig. 7, if both nanosized particles and microsized particles are incorporated in the MMM from the content of 1–5 wt.%, the water flux significantly increases compared to that through the pure PVA membrane.

The driving force of the permeating species is known to be the fugacity difference across the membrane, which is generally proportional to the partial pressure difference [13].

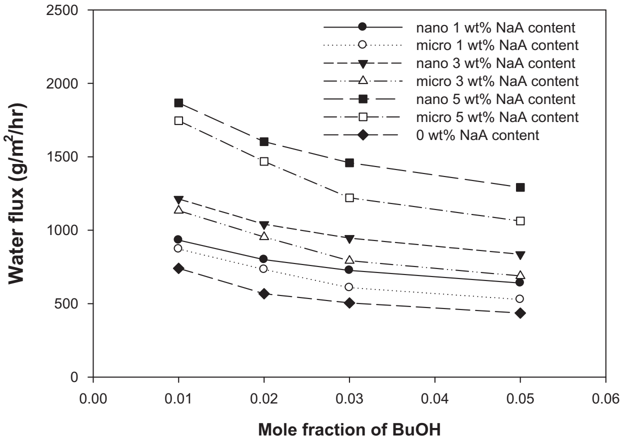


Fig. 7. Water flux through the MMM prepared with different zeolite content as a function of feed *n*-butanol concentration.

In Table 1, the driving force of water is summarized for the given concentrations of water in a feed solution and in a permeate through the MMM prepared with 1 wt.% nanosized NaA particles. As denoted in Table 1, the driving force of water can be written in $x_w P_{wf}^{*} - y_w P_p$. Even if the mole fraction of *n*-butanol is slightly changed from 0.01 to 0.05, the driving force of water significantly decreases, resulting in a decrease of the water flux.

When the NaA zeolite particles are dispersed in the MMM, it is expected that the water flux will be increased since the NaA zeolite is known to have a strong affinity to water. As seen in Fig. 7, the flux of water through the MMM was observed to be in the range from 930 to 1860 kg/m^2/h, depending on both the weight percent of the NaA zeolite particles in the MMM and the concentration of water in a feed solution. In other words, the water flux significantly increased by 25–135% at the typical *n*-butanol concentration of 0.01, compared to that through the pure PVA membrane. Furthermore, at the same weight percent of NaA zeolite particles in the MMM, the flux of water was found to be pretty much influenced by the size of NaA particles. For example, with 1 wt.% of zeolite particles in the MMM, the flux of water increased 7% when the microsized particles were replaced with the nanosized particles. On the other hand, the increment of water flux was 20% in the case of 5 wt.% in the MMM.

These permeation phenomena can be explained as follows. The sorption of water molecules in the MMM could be enhanced, since the NaA zeolite shows quite strongly hydrophilic as shown in Fig. 8, in which a

Table 1
Driving forces of water across MMM at 25℃

x_w	P^*_{wf} (mmHg)	$x_w P^*_{wf}$ (mmHg)	$y_w P_p$ (mmHg)	$x_w P^*_{wf} - y_w P_p$ (mmHg)
0.95	23.756	2.25×10	2.998	1.96×10
0.97	23.756	2.30×10	2.995	2.00×10
0.98	23.756	2.33×10	2.990	2.03×10
0.99	23.756	2.35×10	2.982	2.05×10

The MMM was prepared with 1 wt.% nano sized NaA particles; P^*_{wf} represents the vapor pressure of water; P_p denotes the pressure of the permeate side.

postulated permeation mechanism of water is schematically drawn through the MMM. The sorption sites of the NaA particles will be increased when the weight percent of NaA particles increases, and as a result, the enhancement of water flux will become more significant. Since there are well-developed micropores of 0.4 nm in a NaA zeolite crystal, the water molecules of 0.264 nm in kinetic diameter are expected to be adsorbed and diffused through those pores. When the NaA particles are dispersed in the MMM, the water molecules can diffuse through the free volume formed between polymer matrix as well as through the pores in the NaA zeolite particles. The zeolite particles may play a role to provide the larger free volume through which the water molecules can diffuse more easily than without the particles, leading to the increment of the water flux. If nanosized NaA particles are dispersed in the MMM instead of microsized NaA particles, the surface area of the particles will be much more increased, providing the larger contact area to the water molecules. Therefore, it is expected that the higher flux can be obtained compared to that through the MMM where the microsized NaA particles are dispersed. For example, the microsized zeolite filled MMM showed the water flux ranged between 528 g/m^2/h and 1,062 g/m^2/h at 0.05 mol fraction of *n*-butanol in a feed aqueous solution. On the other hand, the nanosized zeolite filled MMM showed the water flux between 640 g/m^2/h and 1,291 g/m^2/h at the same conditions. Also, when the weight percent of the NaA zeolite particles increased from 1 to 5 wt.%, the flux of water was approximately increased by a factor of 2.

Fig. 9 shows that *n*-butanol fluxes through the MMM are displayed as a function of the mole fraction of *n*-butanol. The flux of *n*-butanol increases as the mole fraction of *n*-butanol in a feed solution increases, since the driving force increases as mentioned before. Table 2 shows the driving force of *n*-butanol across the MMM. Even though the MMMs are quite hydrophilic, the *n*-butanol flux slightly increases as the mole fraction of *n*-butanol in a feed solution increases up to 0.05. This is understandable as water molecules

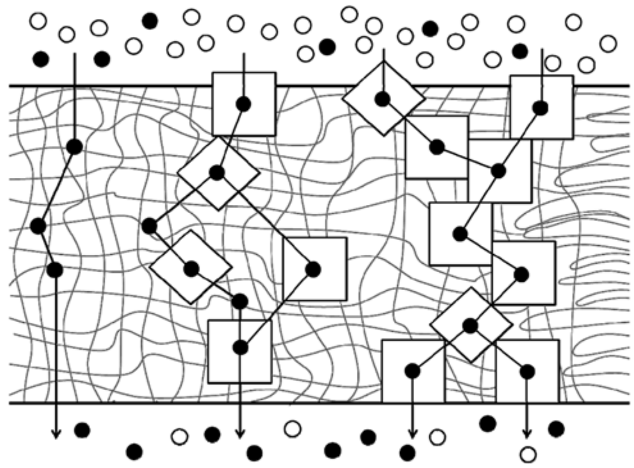


Fig. 8. Postulated permeation mechanism of water through the MMM, water (●) and *n*-butanol (○).

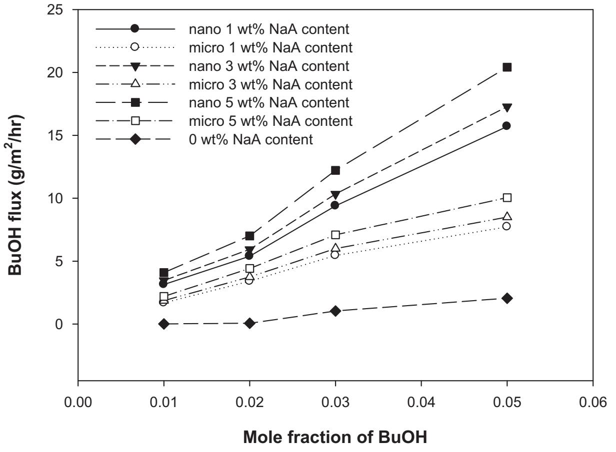


Fig. 9. *n*-butanol flux through the MMM prepared with different zeolite content as a function of feed *n*-butanol concentration.

Table 2
Driving forces of *n*-butanol across MMM at 25℃

x_b	P^*_{bf} (mmHg)	$x_bP^*_{bf}$ (mmHg)	y_bP_p (mmHg)	$x_bP^*_{bf} - y_bP_p$ (mmHg)
0.01	6.109	0.061	1.80×10^{-2}	4.31×10^{-2}
0.02	6.109	0.122	9.53×10^{-3}	1.11×10^{-1}
0.03	6.109	0.183	4.98×10^{-3}	1.78×10^{-1}
0.05	6.109	0.305	2.49×10^{-3}	3.03×10^{-1}

The MMM was prepared with 1 wt.% nano sized NaA particles; P^*_{bf} represents the vapor pressure of *n*-butanol. The vapor pressure was estimated using the Antoine equation.

absorbed in the MMM will swell the MMM, resulting increased free volume and polymer chain flexibility which would enhance the *n*-butanol permeation in addition to the effect of the driving force. At a low concentration of *n*-butanol in a feed solution, the water molecules are preferentially adsorbed in both the PVA matrix and the pores of the NaA zeolite particles in the MMM, leading to the blockage of adsorption of *n*-butanol molecules, which results in a very low permeate of *n*-butanol. Therefore, the flux of *n*-butanol is quite small. In general, the *n*-butanol flux is two order of the magnitude smaller than the water flux. As the weight percent of the NaA zeolite particles in the MMM increases, the flux of *n*-butanol also increases. As mentioned before, the zeolite particles dispersed in the MMM are thought to play a role increasing the free volume, leading to the facilitation of *n*-butanol flux.

Fig. 10 shows total fluxes through the MMM as a function of the mole fraction of *n*-butanol in a feed solution. The total flux is comprised of the water flux and the *n*-butanol flux. Since the *n*-butanol flux is two order of the magnitude smaller than the water flux, the total flux will be approximately the same as the water flux. As mentioned before, the water flux is mainly affected by the weight percent of the NaA zeolite particles in the MMM and the size of the NaA zeolite particles. With the same reasons as for the water flux, the total flux is expected to be affected, resulting in the same permeation behavior as shown in Fig. 7. For example, at the 0.01 mol fraction of *n*-butanol in a feed solution, the total fluxes were found to be 935 g/m^2/h and 1871 g/m^2/h while the water fluxes were observed to be 932 g/m^2/h and 1866 g/m^2/h when the weight percent of nanosized NaA zeolite particles changed from 1 wt.% to 5 wt.% in the MMM, respectively. It can be said that there is no significant difference between the total flux and the water flux.

Fig. 11 shows the separation factor for water with respect to *n*-butanol through the MMM. The separation factor for the MMM continuously decreases as the mole fraction of *n*-butanol increases. If the zeolite particles are added to the pure PVA matrix to form

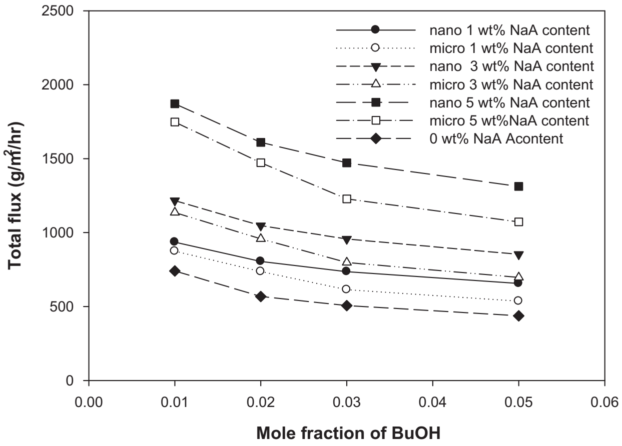


Fig. 10. Total flux through the MMM prepared with different zeolite content as a function of feed *n*-butanol concentration.

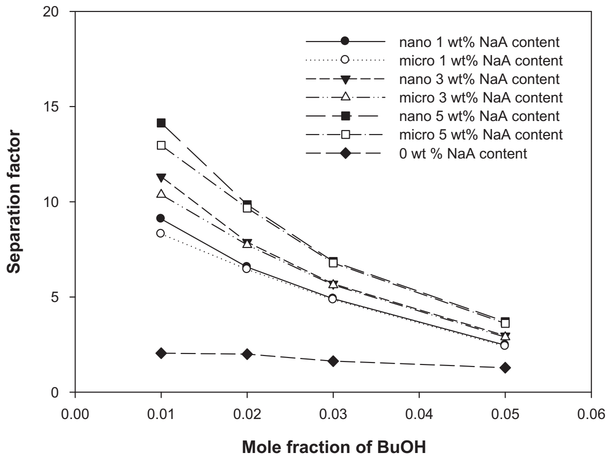


Fig. 11. Separation factor of water over *n*-butanol through the MMM.

the MMM, the separation factor is shown to be increased. Also, when the nanosized NaA particles is used instead of the microsized NaA particles, the separation factor also slightly increases. These phenomena can be explained using Eq. 2, which represents how to obtain the separation factor. For instance, as the concentration of *n*-butanol increases from 0.02 to 0.05 mol fraction with the MMM containing 1 wt.% of nanosized NaA particles, the mole fraction of water in the permeate decreases from 0.9969 to 0.9791. According to Eq. 2, at the *n*-butanol concentration of 0.02 mol fraction, the separation factor can be described as $\frac{0.9969/0.0031}{0.98/0.02} = \frac{B}{A}$ equivalent to 6.6. On the other hand, at the *n*-butanol concentration of 0.05 mol fraction, the separation factor is written as $\frac{0.9791/0.0209}{0.95/0.05} = \frac{D}{C}$ which is about 2.5. When the denominator of A is compared to the denominator C, the magnitude of the denominator C is 2.6 times smaller than that of the denominator A whereas the numerator D is 6.9 times smaller than the numerator B. As a result, the decrease of the numerator is much larger than the decrease of the denominator, resulting in the decrease of the selectivity by a factor of 2.6. The separation factor is said to be significantly affected by a small change of the *n*-butanol concentration, which causes relatively a large change of the *n*-butanol flux even if its absolute magnitude is small.

It is interesting to compare the separation factors of the PVA membrane and the MMM with 5 wt.% nanosized NaA particles: 2.04 and 24.14 at 0.01 mol fraction of *n*-butanol in a feed solution, respectively. Adding the nanosized NaA particles resulted in the increment of the separation factor by a factor of 12. It is understandable because the water flux through the MMM is much larger than that through the pure PVA membrane as shown in Fig. 7. According to Eq. (2), the numerator through the MMM is much larger than that through the pure PVA membrane whereas the denominators of both membranes are the same, resulting in the increase of the separation factor. In other words, by dispersing the small amount of NaA particles in the MMM, the high separation factor can be obtained due to the high increment of the water flux.

Also, it is of importance to take a look at the effect of the weight percent of the NaA zeolite particles on the separation factor. At a typical *n*-butanol concentration of 0.01 mol fraction, the separation factor through the MMM with 5 wt.% with nano NaA particles is found to be 24.14 and that through the MMM with 1 wt.% with nano NaA particles is 16.09, indicating that the separation factor increases 1.5 times by simple addition of the nanosized NaA particles. This separation behavior is understood since the water flux through the MMM with a higher wt.% of the particles is larger than with a lower wt.% of the particles shown in Fig. 7, resulting in a higher separation factor. The more added NaA particles are thought to provide the larger surface area through which the more water molecules might be adsorbed and diffused more easily.

Finally, it is interesting to note the effect of the NaA particle size on the separation factor while the weight percent of the NaA particles in the MMM is kept constant. Initially, it is expected that the separation factor through the MMM with the nanosized NaA particles will show higher than through the MMM with the microsized NaA particles due to the difference in the surface area. However, it is observed that the separation factor is slightly 5% increased by changing the particle size from the micro to the nano. Nevertheless, the nanosized NaA particles will be useful to prepare the MMM as thin as possible

4. Conclusions

The MMM was prepared using both nanosized NaA zeolite particles and microsized NaA zeolite particles dispersed in the PVA matrix. The nanosized NaA zeolite particles were synthesized in the laboratory and they were used to prepared the MMM. Using the synthesized MMM, the pervaporative separation of water from its *n*-butanol aqueous solution was experimentally carried out: the *n*-butanol concentration changed from 0.01 to 0.05 wt.% while the pressure of permeation side was kept about 3 mm Hg.

The weight percent of the NaA zeolite particles in the MMM varied between 0 and 5 wt.%. The effect of the NaA zeolite particles was observed that the flux of water through the MMM was a factor of 2.5 increased compared to the pure PVA membrane at the typical operation condition. When the nanosized particles were dispersed in the MMM instead of the microsized particles, the flux of water was approximately 20% increased, compared to that through the MMM containing the microsized NaA particles. In addition, the separation factor of water was 5% increased.

The synthesized MMM showed a fairly high flux and a good separation factor for water from the *n*-butanol aqueous solution. This result indicates that the MMM prepared with nanosized NaA particles could have a potential to be used to remove water from the *n*-butanol fermentation broth solution.

Symbols

A — effective membrane area (m^2)
P^*_{bf} — vapor pressure of *n*-butanol at 25℃
P_p — pressure in permeate (mmHg)
P^*_{wf} — vapor pressure of water at 25℃
t — permeation time (h)
W — weight of permeate (g)
x_b — mole fraction of *n*-butanol in feed
x_w — mole fraction of water in feed
y_b — mole fraction of *n*-butanol in permeate
y_w — mole fraction of water in permeate

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