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Evaluation of pervaporation condition and synthesis gels for NaA zeolite membranes

Mansoor Kazemimoghadam*, Toraj Mohammadi

Research Lab for Separation Processes, Faculty of Chemical Engineering, Iran University of Science and Technology, Narmak, Tehran, Iran
Tel. +98 (21) 9676620; Fax: +98 (21) 9676620; email: mzkazemi@iust.ac.ir

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ABSTRACT

NaA zeolite membranes were synthesized on the mullite supports. Effects of crystallization time and temperature on the membrane structure and performance of NaA zeolite membranes have been investigated. Molar composition of the starting gel of nano NaA membranes were $SiO_2/Al_2O_3 = 0.8–3.2$, $Na_2O/Al_2O_3 = 1.6–4.6$, and $H_2O/Al_2O_3 = 50–200$. X-ray diffraction patterns of the membranes exhibited peaks corresponding to the support and the zeolite. Morphology of the supports subjected to crystallization were characterized by Scanning electron microscopy. Separation performance of NaA zeolite membranes was studied for water–Ethanol mixtures using pervaporation in dead end and cross-flow method. The membranes showed good selectivity towards water in the water–ethanol mixtures. Water permeates faster because of its preferential adsorption into the nanopores of the hydrophilic zeolite membrane. The membrane exhibits a hydrophilic behavior, with a high selectivity towards water and a good flux. The best flux and separation factor of the membranes were 0.624 kg/m^2 h and 10,000, respectively. Effects of operation condition (temperature, rate, and pressure) on the membrane performance have been investigated for NaA zeolite membranes grown onto seeded mullite supports.

Keywords: Nano; NaA; Pervaporation; Zeolite membrane; Synthesis parameters

1. Introduction

Ethanol is a very important and commonly used solvent in biopharmaceutical and chemical industries. However, it forms an azeotrope with water once it reaches 89.4 mol% at 78°C and atmospheric pressure. This mixture is hard to be separated by using normal distillation process and can only be done through azeotropic distillation. However, azeotropic distillation is more energy-consuming than conventional distillation. Apart from high-energy consumption for azeotropic distillation, benzene, a highly carcinogenic and toxic substance, which is used as an azeotropic dehydrating agent in many plants, is a major health concern. Pervaporation (PV) is an economical separation technique compared to conventional separation methods such as distillation especially in processes involving azeotropes, isomers and removal or recovery of trace substances. Due to its high separation efficiency and flux rates, PV results in energy cost saving and safe operation. In this regard, PV eliminates the use of toxic materials and is a promising alternative for

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*Corresponding author.

energy-consuming distillation processes in separating azeotropic mixtures. Table 1 shows energy consumptions required by different separation methods in ethanol dehydration. In terms of energy requirement, PV is an obvious choice in ethanol–water separation [1–5].

Furthermore, PV has several advantages over traditional distillation: (1) reduced energy demand because only a fraction of the liquid that needs to be separated is vaporized, (2) simple equipment since only a vacuum pump is used to create a driving force, and (3) lower capital cost. Thus, relatively mild operation conditions and high effectiveness make PV an appropriate technique for such separations. As a result, most PV studies have been focused on the dehydration of organic mixtures [6].

In PV, the feed mixture is contacted with a nonporous permselective membrane. Separation is, explained by the steps of sorption into, diffusion through and desorption from the membrane. The latter is usually considered fast and taking place at equilibrium, while diffusion is kinetically controlled and the slowest step of the process. Permeation is dependent on sorption and diffusion steps. The driving force for the separation is created by maintaining a pressure lower than the saturation pressure on the permeate side of the membrane. The mechanism of separation is usually explained in terms of sorption–diffusion processes. Polymeric membranes are not generally suitable for applications involving harsh chemicals due to membrane chemical instability. However, a recent development of chemical-and-temperature-resistant hydrophilic ceramic membranes has made it possible to overcome the limitations of hydrophilic polymeric membranes [7–9].

Zeolites are microporous crystalline materials with a uniform pore size distribution on a molecular scale and with high thermal and chemical stability. A membrane separation system that takes advantage of the adsorption and molecular sieve properties of zeolites requires a continuous zeolite membrane layer. Zeolite membranes have been studied and developed for over 15 years to apply them to separating processes in industry, because they have higher thermal and chemical properties compared with those of polymer membranes [10–12].

Table 1
Energy requirements for ethanol dehydration

Purification (Wt.%)	Energy required (kJ/kg EtOH)	Process
8.0–99.5	10,376	Distillation
95.0–99.5	3,305	Azeotropic distillation
95.0–99.5	423	PV

In this study, Nanopore NaA zeolite membranes were fabricated and then used to separate water/Ethanol mixtures. Zeolite NaA layers were coated on external surface of porous tubular mullite supports using hydrothermal method. These membranes were successfully used for the dehydration of water/Ethanol mixtures.

2. Zeolite structure and transport mechanisms

The hydrophilic membranes used in this research were composite zeolite NaA membranes. The membranes were made of an active NaA layer, deposited on a ceramic porous mullite support. The active NaA layer is responsible for high separation factors achieved in PV of Ethanol mixtures. The structure of zeolite NaA is shown in Fig. 1.

As shown in Fig. 1, the aluminosilicate framework of zeolite NaA is generated by placing truncated octahedrons (b-cage) at eight corners of a cube and each edge of the cube is formed by joining two b-cages by a D4R linkage. Each b-cage encloses a cavity with a free diameter of 0.66 nm and each unit cell encloses a larger cavity (a-cage) enclosing a free diameter of 1.14 nm. There are two interconnecting, three-dimensional channels in zeolite NaA: (i) connected a-cages, 1.14 nm in diameter, separated by 0.42 nm apertures; and (ii) b-cages, alternating with a-cages separated by 0.22 nm apertures. Thus, molecules smaller than 0.42 nm in diameter can diffuse easily through the nanopores of the zeolite. In addition, position of sodium ions in unit cells is important since these ions act as the sites for water sorption and transport through the membrane. For a typical zeolite, a unit cell having the composition $Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$ and eight (out of 12) sodium ions are located inside an a-cage and four ions are located in b-cages.

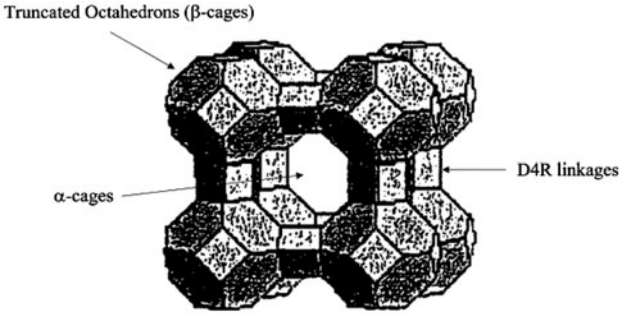

Fig. 1. Repeating unit of zeolite NaA.

Transport of solvent species (mainly water) through the zeolite matrix comprises of three steps: (i) strong adsorption of the species into a cage from feed side, (ii) surface diffusion of the species from cage to cage, and (iii) vaporization of the species to permeate side. Normally, any physical adsorption process includes both van der Waals dispersion–repulsion forces and electrostatic forces comprising of polarization, dipole, and quadrupole interactions. However, since the zeolites have an ionic structure, the electrostatic forces become very large in the adsorption of polar molecules like H_2O. This effect is manifested in the fact that the heat of adsorption of water into zeolitic adsorbents is unusually high (25–30 kcal/mol).

3. Experimental

3.1. Support preparation

In ceramic membranes, thin dense layers are usually deposited over porous tubular supports (14 mm outer diameter, 8 mm inner diameter, and 10 cm length). The porous supports provide mechanical strength for the thin selective layers. Porous supports can be made from alumina, cordierite, mullite, silica, spinel, zirconia, other refractory oxides, and various oxide mixtures, carbon, sintered metals, and silicon carbide.

In this research, mullite supports have been prepared from kaolin clay. Kaolin is thermally converted to mullite via high temperature calcinations. The reaction takes place when kaolin is utilized as the sole source of silica and alumina. The reaction can be represented by the following equation:

$$3(Al_2O_3 \cdot 2SiO_2) \longrightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2$$

Free silica ($4SiO_2$) is generated because of this conversion. The free silica has been leached out and then porous mullite bodies have been prepared. Mullite has several distinct advantages over other materials. Since kaolin is heated to high temperatures to achieve the mullite conversion reaction, strong inter-crystalline bonds between mullite crystals are formed and this results in excellent strength and attrition. Leaching time depends on several factors including:

(1) the quantity of free silica to be removed,
(2) the porosity of body prior to leaching,
(3) the concentration of leaching solution, and
(4) the temperature.

Kaolin (SL-KAD grade) has been supplied by WBB cooperation, England. Analysis of the kaolin is listed in Table 2.

Table 2
Analysis of kaolin clay

Component	Percent (%)	Phases	Percent (%)
SiO_2	51.9	Kaolinite	79
TiO_2	0.1	Illite	8
Al_2O_3	34.1	Quartz	10
Fe_2O_3	1.4	Feldspar	3
K_2O	0.8	Total	100
Na_2O	0.1		
LOI	11.6		
Total	100		

Cylindrical-shaped (tubular) bodies (ID: 10 mm, OD: 14 mm, and *L*: 15 cm) have been conveniently made by extruding a mixture of about 75–67% kaolin and 25–33% distilled water. Suitable calcinations temperatures and periods are those at which kaolin converts to mullite and free silica. Good results have been achieved by calcining for about 3 h at temperatures of about 1,250°C [13,14].

Free silica has been removed from the calcined bodies after leaching by strong alkali solutions. Removal of the silica causes mesoporous tubular supports to be made with very high porosity. Free silica removal has been carried out using aqueous solutions containing 20% by weight NaOH at a temperature of 80°C for 5 h. Supports have been rinsed using a lot of hot distilled water for a long time in order to remove the all remaining NaOH. Porosity of the supports before leaching is 24.3%, while after treatment it increases to 49%. Flux of the supports before and after free silica removal at 1 bar and 20°C are $6\,kg/m^2h$ and $10\,kg/m^2h$, respectively. Porosity of the supports has been measured by water absorption method. Phase identification has been performed by X-ray diffractometry (Philips PW1710, Philips Co., Netherlands) with CuK radiation.

3.2. Zeolite membrane synthesis

3.2.1. Coating of the support with seeds

Adding seed crystals to this crystallization system has resulted in increased crystallization rate. The enhanced rate might be due to simply increasing the rate at which solute is integrated into the solid phase from solution due to the increased available surface area, but also might be the result of enhanced nucleation of new crystals. The secondary nucleation mechanism referred to as initial breeding results from microcrystalline dust being washed off seed crystal surfaces in a new synthesis batch. These microcrystalline fragments grow to observable sizes, and result in greatly enhanced crystallization rates due to the significantly increased crystal surface area compared to the unseeded system. Consequently, it is to be expected that addition of seed crystals to a synthesis system will introduce sub-micron-sized crystallites into the system that will serve as nuclei.

Porous mullite tubes as describe above have been used as supports. External surface of the supports has been polished with 600 grit-sand papers and then they have been washed and cleaned in boiling distilled water for 5 min to remove loose particles created during polishing. Then, the supports have been dried at 100°C for 3 h in air.

In order to coat a thin and uniform zeolite membrane layer over the mullite support, nucleation seeds should be small and uniform in size. To inhibit formation of the zeolites into the support pores, the seeds should not be too small to penetrate into the pores. High-purity nucleation seeds (2μm in size) have been synthesized by hydrothermal method [15]. The seeds should be dispersed homogeneously over the support surface and the amount of seeds should not be too much. Otherwise, the synthesized zeolite membrane layer becomes heterogeneous or too thick. The seeded supports have been prepared by soaking the mullite supports in an 8% NaA zeolite suspension once for 1 min. The 8% NaA zeolite suspension has been prepared by mixing 8 g NaA zeolite in 92 ml distilled water. After soaking, the supports have been dried at 100°C for 3 h in air.

3.2.2. *Zeolite NaA synthesis*

The NaA zeolite membranes were prepared by *in situ* crystallization on the outer surface of the porous mullite tubes. This source was sodium silicate and the Al source was sodium aluminate. Synthesis solution was prepared by mixing aluminate and silicate solutions. NaOH was dissolved in distilled water. The solution was divided into two equal volumes and kept in polypropylene bottles. Aluminate solution was prepared by adding sodium aluminate to one part of the NaOH solution. It was mixed until cleared. Silicate solution was prepared by adding sodium silicate to another part of the NaOH solution. Silicate solution was then poured into aluminate solution and well mixed until a thick homogenized gel was formed. Molar composition of the starting gel of the NaA zeolite membranes was $SiO_2/Al_2O_3 = 0.8–3.2$, $Na_2O/Al_2O_3 = 1.6–4.6$, and $H_2O/Al_2O_3 = 50–200$ [16–19]. Two ends of the supports were closed with rubber caps to avoid any precipitation of the zeolite crystals on the internal surface of the supports during membrane synthesis. The seeded supports were placed vertically in a Teflon autoclave. The solution was carefully poured in the autoclave and then the autoclave was sealed. Crystallization was carried out in an oven at temperatures of 70, 90, 100, 110, and 130°C for 1, 2.5, 3, 4, and 5.5 h, respectively. Then, the samples were taken and the synthesized membranes were washed several times with distilled water. The samples were then dried at room temperature for 12 h in air. The Ethanol mixtures (90 wt.%) were used and experiments were carried out at room temperature (25°C) within a period of 30–60 min. Permeate concentrations were measured using GC (TCD detector, Varian 3400, carrier gas: hydrogen, column is polyethylene glycol, sample size: 5 micron, column and detector temperatures: 120–150°C, detector flow rate: 15 ml/min, carrier flow: 5 ml/min, column pressure: 1.6 kPa, GC input pressure: 20 kPa). Performance of PV was evaluated using values of total flux ($kg/m^2 h$) and separation factor (dimensionless).

4. PV tests

The zeolite membranes have been used for long-term dehydration of Ethanol. The experiments have been carried out at a temperature of 30°C and a pressure of 1.5 mbar at the permeate side, within a period of 30–60 min.

The PV setups are presented in Figs. 2(a), 2(b) and 3. Any change of feed concentration due to

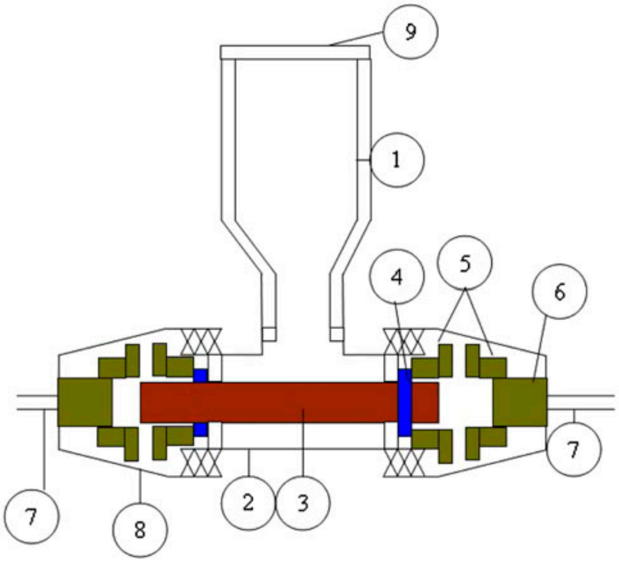

Fig. 2(a). PV cell: 1—feed tank; 2—membrane module; 3—membrane; 4—O-ring; 5—Teflon fitting; 6—stainless steel vacuum fitting; 7—vacuum hose; 8—cap; and 9—feed tank cap.

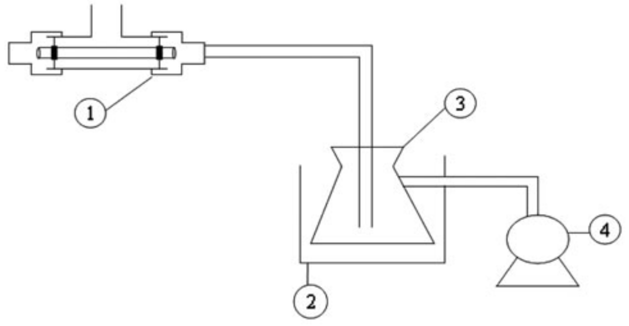

Fig. 2(b). PV setup (dead end): 1—PV cell; 2—liquid nitrogen trap; 3—permeate container; and 4—three stage vacuum pump.

permeation is negligible because the amount of permeate is small (max 2 ml) compared to total feed volume in the system (0.5 L). A three-stage diaphragm vacuum pump (vacuubrand, GMBH, Germany) has been employed to evacuate the permeate side of the membrane to a pressure of approximately 1.5 mbar while the feed side has been kept at room pressure. The permeate side has been connected to a liquid-nitrogen trap via a hose to condense the permeate (vapor). Permeate concentrations have been measured by a GC (TCD detector, Varian 3400).

Performance of PV is usually evaluated by total flux ($kg/m^2 h$) and separation factor (dimensionless). Separation factor of any organic aqueous solution can be calculated from the following equation:

$$\text{Separation factor}(\alpha) = \frac{[X_{H_2O}/X_{\text{Organic}}]_{\text{permeate}}}{[X_{H_2O}/X_{\text{Organic}}]_{\text{feed}}}$$

where X_{H_2O} and X_{organic} are weight fractions of water and organic compound, respectively.

5. Results and discussion

5.1. Gel composition

As mentioned earlier, zeolites could be synthesized by the hydrothermal method. The versatility of hydrothermal chemistry owes much to the mineralizing role of water. The factors that promote reactivity in aqueous magmas include:

(1) Stabilization of porous lattices as zeolites by acting as space fillers, referred to above.
(2) Through its presence, especially at high pressures, water may be incorporated into hydrous glasses, melts, and solids. Through chemisorptions into siliceous materials, Si–O–Si, and Al–O–Si, bonds hydrolyze and reform. Chemical reactivity is enhanced and magma viscosity is lowered.
(3) High pressures of water can modify phase equilibrium temperatures.
(4) Water is a good solvent, a property that assists disintegration of solid components of a mixture and facilitates their transport and mixing.

Water is important as a guest molecule in zeolite structures with relatively high Al contents and consequently, aqueous media favor their formation while salts have a parallel role in the stabilization of zeolite structure. In general, the zeolitic water can be removed leaving the unchanged hydrous zeolite. In hydrothermal systems, the good solvent powers of water promote mixing, transport materials, and facilitate nucleation and crystal growth. Water stabilizes zeolite structures by filling the cavities and forming a type of solid solution. The stabilizing effect is such that the porous aluminosilicates will not form in the absence of a guest molecule, which may be a salt molecule as well as water. However, the water concentration or the degree of dilution is important for the synthesis of HS, which can crystallize out of gels with an extremely wide range of H_2O/Al_2O_3 ratios (from 500 to 1,500).

The Na_2O or alkalinity of the media plays a vital role in crystal growth, materials synthesis/preparation, and processing, overall. It influences the super saturation, kinetics, morphology, shape, size, and crystallinity of the particles or materials as the OH^- anions fulfill the crucial role of mineralizing agent. The Na_2O is influenced by the reactants and their concentrations/ratios, followed by temperature and time. Further, with the introduction of organics, the alkalinity changes rapidly in the system, hence, alkalinity is the key parameter in determining the crystallization rate. An increase in OH concentration will generally bring about an accelerated crystal growth and a shortened induction period before viable nuclei are formed. In zeolite synthesis, pH of the alkaline solution is usually between 8 and 12. The major role of pH is to bring the Si and Al oxides or hydroxides into solution at an adequate rate.

To study effects of gel composition on Nanopore NaA zeolite membrane performance, the membranes were synthesized at different compositions ($SiO_2/Al_2O_3 = 0.8–3.2$, $Na_2O/Al_2O_3 = 1.6–4.6$, and $H_2O/Al_2O_3 = 50–200$) for duration 3 h and temperature 100°C. It must be also mentioned that three samples were prepared for each condition. The results were presented on average and the maximum deviation was less than 3%.

As seen in Table 3, NaA zeolite membranes have been successfully synthesized in ranges of $SiO_2/Al_2O_3 = 0.8$ to $SiO_2/Al_2O_3 < 2.4$, and $Na_2O/Al_2O_3 = 1.6–4.6$, $H_2O/Al_2O_3 > 100$ to $H_2O/Al_2O_3 = 200$. In $H_2O/Al_2O_3 < 100$ ratio, NaA zeolite membranes have not been successfully synthesized, because gel composition does not have enough water for the synthesis of a homogenous gel. Also, in $SiO_2/Al_2O_3 > 2.4$ ratio causes NaA zeolite to transform to other zeoliets such as NaX. It must be mentioned that 10,000 is the highest measurable value using the GC at 90 wt.% Ethanol concentration as shown in Table 3.

5.2. Temperature and time

Temperature and time have a positive influence on the zeolite formation process, which occurs over a considerable range of temperatures. A rise in temperature will increase both the nucleation rate and the linear growth rate; hence, the crystallinity of the samples normally increases in time. As far as time is concerned, zeolite synthesis is governed by the occurrence of successive phase transformations. The thermodynamically least favorable phase will crystallize first and will be successively replaced in time by more stable phases. The best example is the crystallization sequence of amorphous → NaA → HS.

The temperature, however, can also influence the type of product that has to be crystallized. A rise in temperature leads to the crystallization of more dense products as the fraction of water in the liquid phase, which has to stabilize the porous products by filling the pores, will drop. Therefore, the existence of an upper limit for the formation of zeolites is to be expected. The use of nonvolatile pore space occupying (filling) species would, in principle, allow a high-temperature synthesis of open, porous structures. Temperature can obviously affect the rate of nucleation and crystal growth.

The linear rates of crystal growth and rates of nucleation both increase with rising temperatures.

To study effect of crystallization time and temperature on NaA zeolite membrane performance, the membranes were synthesized at different temperatures (70, 90, 100, 110, and 130°C) for different times (1, 2.5, 3, 4, and 5.5 h). As seen in Table 3, increasing crystallization time decreases flux (samples 18 and 19). However, there is no change in separation factor. This may be because at a longer crystallization, time a thicker membrane layer is formed. This causes flux to decrease. This shows that these membranes behave very high selectivity. In this work, any test (preparation membrane and PV test) carried out three times. The results show that short crystallization time (1 h) is

Table 3
Flux and separation factor of Nanopore NaA zeolite membranes (dead end)

Sample	Number of coating	SiO_2/Al_2O_3	Na_2O/Al_2O_3	H_2O/Al_2O_3	*t* (h)	*T* (°C)	Ethanol (%)	Flux ($kg/m^2 h$)	Separation factor
1	1	0.8	3.165	128	3	100	90	0.223	>10,000
2	1	1.6	3.165	128	3	100	90	0.227	>10,000
3	1	2.4	3.165	128	3	100	90	0.539	1
4	1	3.2	3.165	128	3	100	90	0.032	41
5	1	1.926	1.6	128	3	100	90	0.042	>10,000
6	1	1.926	2.6	128	3	100	90	0.047	>10,000
7	1	1.926	3.6	128	3	100	90	0.281	>10,000
8	1	1.926	4.6	128	3	100	90	0.227	>10,000
9	1	1.926	3.165	50	3	100	90	–	1
10	1	1.926	3.165	100	3	100	90	–	1
11	1	1.926	3.165	150	3	100	90	0.114	>10,000
12	1	1.926	3.165	200	3	100	90	0.624	>10,000
13	1	1.926	3.165	128	3	70	90	0.0556	>10,000
14	1	1.926	3.165	128	3	90	90	0.0602	>10,000
15	1	1.926	3.165	128	3	110	90	0.0741	>10,000
16	1	1.926	3.165	128	3	130	90	0.398	>10,000
17	1	1.926	3.165	128	1	100	90	0.970	41
18	1	1.926	3.165	128	2.5	100	90	0.527	>10,000
19	1	1.926	3.165	128	4	100	90	0.247	>10,000
20	1	1.926	3.165	128	5.5	100	90	0.306	2

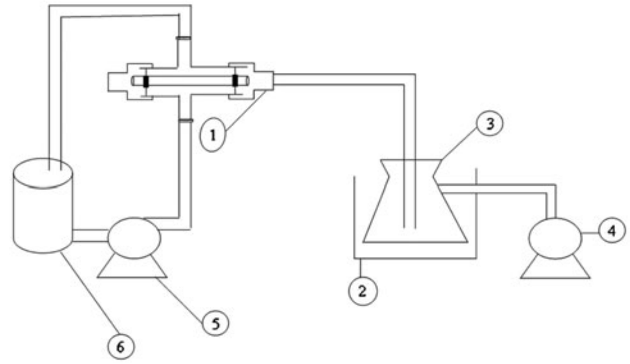

Fig. 3. PV setup cross-flow; 1—feed container and PV cell; 2—liquid nitrogen trap; 3—permeate container; 4—three stage vacuum pump; 5—centrifuge pump; and 6—tank feed.

not enough to make an effective zeolite layer on the support (sample 17). In addition, long crystallization time (5.5 h) causes NaA zeolite to transform to other zeolites such as NaX. As a result, this sample (20) shows poor selectivity. The crystallization time in a range of 2.5–4 h was found to be very effective for making the NaA zeolite layer.

The synthesis procedure was also performed using different temperatures. As seen in Table 3, increasing crystallization temperature increases flux (samples 13–16). In addition, it can be observed that there is no change in separation factor. This may be because at higher crystallization temperature, a thinner layer is formed. It is because, at higher temperatures, NaA zeolite crystals are smaller. This shows that these membranes behave very high selectivity. The results show that a high temperature of 130°C also form zeolite NaA (sample 16). The crystallization temperature in a range of 70–130°C was found to be very effective for making the NaA zeolite layer.

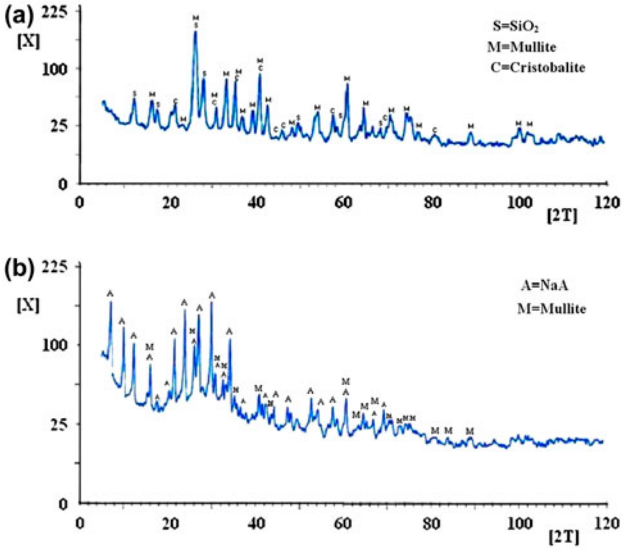

Fig. 4. XRD patterns of (a) the support and (b) the membrane.

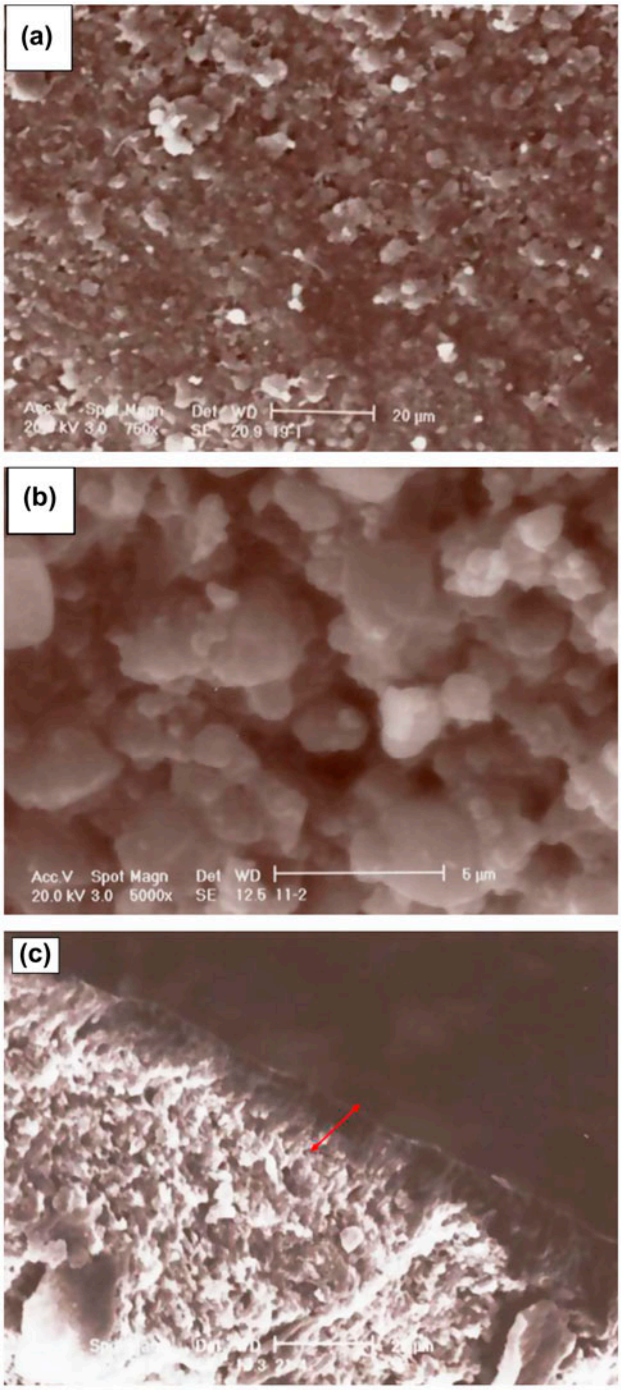

Fig. 5. SEM micrograph of (a) the support; (b) the membrane; and (c) the thickness of membrane on support.

Fig. 4 shows XRD patterns of the mullite support (a) and the NaA zeolite membrane (b). The XRD pattern of NaA zeolite membrane confirms that zeolite NaA crystals were formed. Fig. 5 shows SEM photographs of the mullite support (a) and the NaA zeolite membrane (b). Porous structure of the support and thin layer of the membrane can be easily observed.

5.3. PV-operating conditions

Effect of operating conditions at PV process was evaluated by cross-flow PV pilot. The transmembrane pressure is adjusted between 1 and 3 bar. The feed temperature is varied between 20 and 60°C by means of a small heat exchanger employed into the feed tank. Feed rate is varied between 0.5 and 3 L/min by means of centrifuge pumps and recycles line. Permeate collected in a sample bottle is measured. The outlet flow of the cell can be led out of the system or returned to the tank. A shown in Table 4, effect of feed rate on permeate flux was measured at constant temperature (20°C) and constant pressure (1 bar). Increasing feed rate increases the permeate flux. As shown in Table 4, increasing pressure increases the permeate flux. Increasing rate increases turbulence and hydrodynamic effects cause increase in permeate flux. Temperature is known as a main parameter. Increasing temperature causes an increase in viscosity reduction. Table 4 shows the experimental data for the flux as a function of temperature. As seen, the flux increases with temperature. According to the results, it can be said the optimum-operating conditions were 60°C, 3 bar and 3 L/min.

The study was conducted in all stages of construction and testing of NaA zeolite membranes.

First, support of membrane was prepared using kaolin calcinations process. Then, various formulations of zeolite synthesis gel were investigated and the optimum conditions of synthesis were determined. The effect of temperature and time of synthesis on the performance of the membrane was investigated and the optimal conditions were obtained. Finally, membranes were evaluated using a PV Pilot and effect of various operating conditions such as temperature, pressure, flow, and concentration on membrane performance was investigated.

Table 4
cross-flow results by zeolite membrane

Run	Concentration of ethanol in feed (wt.%)	P (bar)	Q (L/min)	T (°C)	Flux (kg/m^2 h)
1	80	1	0.5	20	1.082
2	80	1	1.5	20	1.407
3	80	1	3	20	1.673
4	80	1	0.5	20	1.082
5	80	2	0.5	20	1.421
6	80	3	0.5	20	1.764
7	80	1	0.5	20	1.082
8	80	1	0.5	40	2.237
9	80	1	0.5	60	2.772

6. Conclusion

Zeolite NaA membranes were synthesized on the porous mullite tubes by hydrothermal method. It was found that according to gel compositions, time, and temperature range, NaA zeolite membranes have been synthesized. The best range-operating condition (time and temperature) for hydrothermal synthesis of nanopore NaA zeolite membrane was 2.5–4 h and 70–140°C, respectively. These membranes showed very good membrane performance for separation of Ethanol /water mixtures. Effect of operating condition at PV process shows that increasing pressure, feed rate, and temperature increase the flux linearly.

References

[1] H. Churl, Y. Ka, G. Jeong, K. Si, M. Young, Synthesis, ethanol dehydration and thermal stability of NaA zeolite/alumina composite membranes with narrow non-zeolitic pores and thin intermediate layer, J. Membr. Sci. 364 (2010) 138–148.

[2] A. Buekenhoudt, C. Dotremont, V. Van Hoof, Performance of Mitsui NaA type zeolite membranes for the dehydration of organic solvents in comparison with commercial Polymeric pervaporation membranes, Sep. Purif. Technol. 48 (2006) 304–309.

[3] F. Cunill, M. Pera-Titus, Preparation of zeolite NaA membranes on the inner side of tubular supports by means of a controlled seeding technique, Catalysis Today 104 (2005) 281–287.

[4] S. Amnuaypanich, J. Patthana, P. Phinyocheep, Mixed matrix membranes prepared from natural rubber/poly(vinyl alcohol) semi- interpenetrating polymer network (NR/PVA semi-IPN) incorporating with zeolite 4A for the pervaporation dehydration of water–ethanol mixtures, Chem. Eng. Sci. 64 (2009) 4908–4918.

[5] Zhen Huang, Yan Shi, Rui Wen, Yu-Hua Guo, Su Jun-Feng, T. Matsuura, Multilayer poly(vinyl alcohol)–zeolite 4A composite membranes for ethanol dehydration by means of pervaporation, Sep. Purif. Technol. 51 (2006) 126–136.

[6] Kiminori Sato, Kazunori Sugimoto, Takashi Nakane, Preparation of higher flux NaA zeolite membrane on asymmetric porous support and permeation behavior at higher temperatures up to 145°C in vapor permeation, J. Membr. Sci. 307 (2008) 181–195.

[7] Yanshuo Li, Hongliang Chen, Jie Liu, Hongbo Li, Weishen Yang, Pervaporation and vapor permeation dehydration of Fischer–Tropsch mixed-alcohols by LTA zeolite membranes, Sep. Purif. Technol. 57 (2007) 140–146.

[8] S. Sorenson, E. Payzant, W. Gibbons, B. Soydas, H. Kita, R. Noble, J. Falconer, Influence of zeolite crystal expansion/contraction on NaA zeolite membrane Separations, J. Membr. Sci. 366 (2011) 413–420.

[9] I. Kresse, J. Springer, Z.K. Zhou, Xin-Gui Li, Effect of temperature and pressure on gas transport in ethyl cellulose membrane, Polymer 42 (2001) 6801–6810.

[10] J. Llorens, M. Pera-Titus, Description of the pervaporation dehydration performance of A-type zeolite membranes: A modeling approach based on the Maxwell–Stefan theory, Catal. Today 118 (2006) 73–84.

[11] M. Pera-Titus, R. Mallad, Preparation of inner-side tubular zeolite NaA membranes in a semi-continuous synthesis system, J. Membr. Sci. 278 (2006) 401–409.

[12] L. Santos, T. Gallego-Lizon, Y.S. Ho, Comparative study of commercially available polymeric and microporous silica membranes for the dehydration of IPA/water mixtures by pervaporation/vapour permeation, Desalination 149 (2002) 3–8.

[13] K. Speronello, 1986-Porous mullite, US Patent No. 4628042.

[14] K. Speronello, 1986-Porous mullite, US Patent No. 4601997.

[15] S. Sridhar, A. Khan, R. Ravindra, Recovery of monomethylhydrazine liquid propellant by pervaporation technique, Ind. Eng. Chem. Res. 39 (2001) 2485–2490.

[16] C. Tellez, J.L. Hang chau, K.L. Yeung, K. Ho, The role of surface chemistry in zeolite membrane formation, J. Membr. Sci. 164 (2000) 257–275.

[17] A. Verkerk, J.T.F. Keurentjes, M.A.G. Vorstman, P. van Male, Properties of high flux ceramic pervaporation membranes for dehydration of alcohol/water mixtures, Sep. Purif. Technol. 22–23 (2001) 689–695.

[18] Sonia Aguado. Jorge Gascón, Jacobus C. Jansen, Freek Kapteijn, Continuous synthesis of NaA zeolite membranes, Microporous Mesoporous Mater. 120 (2009) 170–176.

[19] A. Malekpour, M.R. Millani, M. Kheirkhah, Synthesis and characterization of a NaA zeolite membrane and its applications for desalination of radioactive solutions, Desalination 225 (2008) 199–208.