

ZSM-11 Membranes: Characterization and Pervaporation Performance

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High-quality boron and aluminium-substituted ZSM-11 membranes were prepared on porous tubular supports to separate alcohols from water by pervaporation. The C_1 – C_3 alcohols were preferentially separated from aqueous solutions through the B-ZSM-11 membrane, and the maximum flux was $1.7 \text{ kg/m}^2 \cdot \text{h}$ for a 5 wt.% methanol/water mixture. The alcohol fluxes decreased as the carbon number increased. The methanol/water separation selectivity decreased with pervaporation temperature, but other alcohol/water selectivities increased. All selectivities increased with decreasing alcohol feed concentration. In a range of 1 to 50 wt. % alcohol, the separation selectivities at 333 K for the C_1 – C_3 linear alcohols were higher than vapor/liquid equilibrium selectivities. The highest selectivities observed for methanol/water, ethanol/water, 1-propanol/water, and 2-propanol/water were 28, 97, 34, and 26, respectively, at 1 wt. % alcohol feed concentrations. The separation selectivities were based on both preferential adsorption of alcohols and differences in diffusion rates.

Introduction

Zeolite membranes have advantages, such as better chemical and thermal stability, over polymer membranes. Since Suzuki (1987) patented the first preparation of zeolite membranes in 1987, many types of zeolite membranes have been prepared and used for gas separations and pervaporation. For example, small-pore (A-type) (Myatt et al., 1992), medium-pore (MFI- and FER-type) (Sano et al., 1994; Yan et al., 1995; Nishiyama et al., 1997; Coronas et al., 1997), and large-pore (MOR-, X-, and Y-type) (Nishiyama et al., 1995; Kita et al., 1997; Li et al., 2001a). Membrane preparation was extended to related materials such as crystalline silicoaluminophosphates (SAPO) (Sano et al., 1992; Poshusta et al., 2000).

Most previous studies have focused on silicalite-1 and ZSM-5 membranes, which have the MFI structure. The MFI zeolites have a system of straight channels (pore size: $0.53 \times 0.56 \text{ nm}$) interconnected by zigzag channels (pore size: $0.51 \times 0.55 \text{ nm}$). Cook and Conner (1999), however, reported that molecules that are significantly larger than these dimensions

could fit into the ZSM-5 pores, which they calculated to be 0.62 nm in diameter. The ZSM-11 zeolite and its all-silica version, silicalite-2, have pore sizes that are similar to those for ZSM-5, but they have the MEL structure, which has intersecting straight channels only (pore size: $0.54 \times 0.53 \text{ nm}$). The pores have 10-membered oxygen rings like ZSM-5. Den Exter (1996) was unable to synthesize an MEL membrane as a pure phase, and instead he obtained a mixture of MFI and MEL structures. We (Li et al., 2001b) also reported that mixed ZSM-5 and ZSM-11 membranes were obtained when a crystallization temperature of 443 K was used.

Isomorphous substitution has been shown to be an effective method for modifying the MFI structure, and membranes with boron substituted into the MFI framework membranes had higher $n\text{-C}_4\text{H}_{10}/i\text{-C}_4\text{H}_{10}$ gas-phase selectivities than Al-ZSM-5 membranes (Tuan et al., 2000). The B-ZSM-5 membrane also selectively permeated alcohols from aqueous solutions by pervaporation (Tuan et al., 2002). A boron-substituted ZSM-11 (Si/B = 100) membrane, synthesized by an alkali-free method (Tuan et al., 2001), was effective at separating MEK from aqueous solution by pervaporation. The to-

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tal flux was $0.69 \text{ kg/m}^2 \cdot \text{h}$, and the separation selectivity was 224 at 333 K for a 5 wt. % MEK feed concentration.

Pervaporation has advantages over distillation (Fleming and Slater, 1992), including reduced energy demand (only a fraction of the liquid is vaporized), and relatively inexpensive equipment (only a small vacuum pump is needed to create a driving force). Pervaporation using zeolite membranes has concentrated on organic/water feed mixtures. Water can be separated from mixtures with alcohols by using hydrophilic A- and Y-type zeolite membranes (Ishikawa et al., 1989; Kita et al., 1995, 1997, 2000; Li et al., 2001c). Ishikawa et al. (1989) used an A-type membrane to separate water from ethanol. At 352 K and for a 5 wt. % water feed, the membrane has a total flux of $0.1 \text{ kg/m}^2 \cdot \text{h}$ and a water/ethanol separation selectivity of 1633. Kita et al. (1995), using an A-type membrane, obtained a water/methanol separation selectivity of 2500 with a total flux of $0.23 \text{ kg/m}^2 \cdot \text{h}$ at 323 K for a 5.5 wt. % water feed, and a water/ethanol selectivity of 16,000 with a total flux of $1.1 \text{ kg/m}^2 \cdot \text{h}$ at 348 K for a 5.1 wt. % water feed. In contrast, organics can be separated from aqueous solutions with hydrophobic zeolite membranes (Sano et al., 1994; Liu et al., 1996; Li et al., 2001d).

Methanol/water mixtures have been separated by pervaporation using polymer membranes, but either the separation selectivities or the fluxes were not high (Wesslein et al., 1988). Devaine et al. (1995), using a silicalite-filled membrane (GFT 1170), obtained a separation selectivity of 5 and a methanol flux of about $0.1 \text{ kg/m}^2 \cdot \text{h}$ for a methanol feed concentration of 5.3 wt. %. With a stainless-steel-supported silicalite-1 membrane, Sano et al. (1994), using a 1.8 wt. % methanol feed concentration, obtained a methanol/water selectivity of about 17 with a total flux of about $0.56 \text{ kg/m}^2 \cdot \text{h}$ at 303 K. Liu et al. (1996), using a silicalite-1 zeolite membrane on a stainless-steel tube, obtained selectivities between 11 and 14.3, and total fluxes between 1 and $2.7 \text{ kg/m}^2 \cdot \text{h}$ in a methanol concentration range of 3.5 to 65 wt. % at 305 K.

The separation of ethanol from water is important for ethanol production from biomass. Sano et al. (1994) measured a flux of $0.72 \text{ kg/m}^2 \cdot \text{h}$ and an ethanol/water selectivity of 50 at 333 K through a silicalite-1 membrane. Nomura et al. (1998), using membranes prepared by the same procedure as Sano et al., observed that the ethanol permeate concentration was higher than the vapor/liquid equilibrium concentration for all feed compositions. At 303 K, their maximum selectivity was 62 with a total flux of $0.6 \text{ kg/m}^2 \cdot \text{h}$ for a 4.65 wt. % ethanol feed.

Te Hennepe et al. (1994) used silicalite-filled silicone membranes to separate 1-propanol from aqueous solution. At 333 K and for a 5 wt. % 1-propanol feed, the membrane with a silicalite content of 50% has a total flux of $0.034 \text{ kg/m}^2 \cdot \text{h}$ and a separation selectivity of 25. Separations of 1-propanol and 2-propanol from aqueous solution using a silicalite-1 membrane was reported by Sano et al. (1994). At 333 K and for a 3.3 wt. % propanol feed, the 1-propanol/water selectivity was 76 and the total flux was $0.16 \text{ kg/m}^2 \cdot \text{h}$, whereas the 2-propanol/water selectivity was 36 with a total flux of $0.22 \text{ kg/m}^2 \cdot \text{h}$.

In the current study, Al-ZSM-11 (Si/Al = 600) and B-ZSM-11 (Si/B = 100) membranes were prepared on porous alumina and stainless-steel tubes and characterized by X-ray diffraction, SEM, and pervaporation of *o*-xylene and 1,3,5 tri-

isopropyl benzene (TIPB). These membranes were used to separate alcohol/water mixtures by pervaporation over a range of temperatures and concentrations.

Experimental Methods

Membrane preparation and characterization

Membranes were prepared by *in situ* crystallization onto tubular porous supports (α - Al_2O_3 , $0.2 - \mu\text{m}$ pores, U.S. Filter; stainless steel, $0.5 - \mu\text{m}$ pores, Mott Company). About one cm on each end of the alumina supports was glazed. Non-porous stainless-steel tubes were welded onto each end of the stainless-steel supports to provide a sealing surface for the *o*-rings. Before membrane preparation, the supports were cleaned by brushing the inner surfaces of the tubes and then treating them in an ultrasonic bath that contained D.I. water. The support tubes were then boiled in distilled water for 1 h and dried at 373 K under vacuum for 30 min.

tetra-Butyl-ammonium hydroxide (TBAOH) was used as a template in MEL membrane preparation. The presence of NaOH was necessary for preparation of Al-ZSM-11 membranes because TBA^+ could not compensate for the negative charge created by Al incorporation. The following molar gel compositions were used: $1.25 \text{ (or } 2.5) \text{ Na}_2\text{O} \times 1.5 \text{ TBAOH} \times 19.46 \text{ SiO}_2 \times 0.00162 \text{ Al}_2\text{O}_3 \times 438 \text{ H}_2\text{O}$, where Ludox AS 40 (silica sol) and sodium aluminate ($\text{Na}_2\text{Al}_2\text{O}_4$) were used as the Si and Al sources, respectively. The B-ZSM-11 membranes were prepared by an alkali-free method, and the molar gel composition was $2.5 \text{ TBAOH} \times 0.195 \text{ B(OH)}_3 \times 19.5 \text{ SiO}_2 \times 450 \text{ H}_2\text{O}$. Three solutions were used: solution A contained silica sol; solution B had $\text{TBAOH} + \text{H}_2\text{O}$ (half of the total water amount); and solution C had $\text{NaOH} + \text{Na}_2\text{Al}_2\text{O}_4$ (or $\text{B(OH)}_3 + \text{H}_2\text{O}$ (the other half of the water)). Solution A was added to solution B, and then solution C was added while stirring. To obtain a homogeneous gel, the mixture was stirred at room temperature for 2 h.

The membranes were synthesized on the inside of the stainless-steel tubes. One end of the tube was wrapped with Teflon tape and plugged with a Teflon cap. The vertical tube was then filled with approximately 2 mL of the synthesis gel and left overnight at room temperature. During this time the porous support soaked up almost all the synthesis gel. The tube was again filled with synthesis gel and the other end was then wrapped with Teflon tape and plugged with a Teflon cap. The tube was placed vertically in a Teflon-lined autoclave. For the Al-ZSM-11 membrane, one layer was hydrothermal crystallized at 403 K for 24 h, and then two layers were synthesized at 403 K for 72 h. For the B-ZSM-11 membranes, two layers were synthesized at 403 K for 72 h. After synthesis, the membranes were washed twice with distilled water, dried in a vacuum oven at 373 K, and then calcined in air at 753 K for 8 h with heating and cooling rates of 0.015 and 0.018 K/s, respectively.

X-ray diffraction (XRD) analysis was carried out on powder collected from the bottom of the membrane tubes. A Scintag PAD-V diffractometer with Cu $K\alpha$ radiation was used. Some membranes were broken and analyzed by a SEM (ISI-SX-30) operated at 30 kV. The membrane quality was characterized by pervaporation of *o*-xylene (0.685-nm kinetic diameter) and tri-isopropyl benzene (TIPB, 0.85-nm kinetic

diameter) at 300 K, since these molecules had kinetic diameters that are larger than the zeolite pore diameter. The pervaporation fluxes for membrane M2 were also measured at 330 K. Single-gas permeation rates of $n\text{-C}_4\text{H}_{10}$ and $i\text{-C}_4\text{H}_{10}$ for membrane M5 was measured at 300, 373, 423 and 473 K. For the gas permeation measurements, the membranes were sealed in a stainless-steel module by Viton O-rings with a feed pressure of 222 kPa and a permeate pressure of 84 kPa.

Pervaporation measurements

The pervaporation system was similar to that used by Liu et al. (1996). The membrane was sealed in a brass module with Viton O-rings, and the liquid feed (250 cm³) flowed through the inside of the membrane at a flow rate of 20 cm³/s. The retentate was recirculated by a centrifugal pump to the feed side of the membrane. The system lines near the membrane module were wrapped with heating tape and insulated so that pervaporation could be carried out at elevated temperatures. A thermocouple was placed in the liquid in the center of the membrane, and the temperature was controlled by a temperature controller. A mechanical vacuum pump evacuated the permeate side of the membrane to a pressure of approximately 0.2 kPa, and the pump was then valved off during pervaporation measurements. A liquid nitrogen cold trap condensed the permeate vapor and maintained the vacuum on the permeate side below 0.5 kPa.

The membranes had permeable areas of approximately 5.2 cm² and were calcined for 3 h at 673 K to remove contaminants prior to each run at a given liquid-feed composition. All alcohols were HPLC grade. A permeate sample was collected and weighted every 2 h to determine the total pervaporation flux. Permeate concentrations were measured by off-line GC (Hewlett-Packard 5730A) equipped with a 6-ft PORAPAK-Q packed column and a thermal conductivity detector. The oven and injection temperatures were 333 and 508 K, respectively.

The composition separation selectivity is the same as the separation factor $\alpha_{\text{alcohol/water}} = (y_{\text{alcohol}}/y_{\text{water}})/(x_{\text{alcohol}}/x_{\text{water}})$, where x and y are the weight fractions in the feed and permeate, respectively. The ideal selectivity is the ratio of pure component fluxes. The volatility (vapor/liquid equilibrium selectivity) is defined the same way as the separation factor, but x and y denote the equilibrium mass fractions in the liquid and vapor phase, respectively.

Results

Membrane characterization

The ZSM-11 membranes and their synthesis properties are listed in Table 1. All membranes had TIPB pervaporation fluxes at 300 K that were 5 g/m²·h or less, and the *o*-xylene fluxes were higher. Since the TIPB molecule (0.85 nm) is significantly larger than the MEL pores (0.54×0.53 nm), these membranes apparently contain some nonzeolite pores larger than 0.85 nm. Membranes M1 and M4 (higher NaOH concentration) had much higher *o*-xylene fluxes than membranes M2 and M3 (lower NaOH concentration). Thus, better quality ZSM-11 membranes are obtained when lower NaOH concentrations are used in the synthesis gel. Similarly, Tuan et al. (1999) observed that preparation of ZSM-5 membranes by an alkali-free method yielded better membranes for $n\text{-C}_4\text{H}_{10}/i\text{-C}_4\text{H}_{10}$ separation. The *o*-xylene fluxes at 300 K for most membranes were approximately 10 times the TIPB fluxes, because *o*-xylene is smaller and there were some nonzeolite pores between 0.685 and 0.85 nm. Interestingly, membrane M2 had similar *o*-xylene and TIPB fluxes, perhaps because most of its nonzeolite pores were larger than 0.85 nm. Membrane M6 was prepared by the same procedure as M5, but it was used for pervaporation of a 67 wt % nitric acid/water mixture before being used for the *o*-xylene and TIPB measurements. Membrane M6 apparently had more non-zeolite pores than M5, since both *o*-xylene and TIPB fluxes were higher. At 330 K, the TIPB and *o*-xylene fluxes for membranes M2 and M5 were approximately 30% higher than the fluxes at 300 K. The $n\text{-C}_4\text{H}_{10}/i\text{-C}_4\text{H}_{10}$ ideal selectivity at 300 K was 14 for membrane M5, and decreased linearly with temperature. At 473 K, the selectivity was 5, which indicates the membrane is of reasonable quality.

The XRD patterns of powders collected from the bottom of membranes M1 and M5 are shown in Figure 1. The Al-ZSM-11 powder (Figure 1a) was prepared in the presence of NaOH and seems to be better crystallized than the B-ZSM-11 powder (Figure 1b), which was prepared from an alkali-free gel. Moreover, the background for the B-ZSM-11 powder is noisier, which indicates that some amorphous material formed. All peaks in both XRD spectra match those reported by Szostak (1989) for MEL crystals, and no additional peaks were observed.

The SEM images of membranes M3 and M6 are shown in Figure 2. The surface of the Al-ZSM-11 membrane (Figure 2a) has a continuous layer of intergrown crystals 1–2 μm in

Table 1. ZSM-11 Membrane Properties

Memb.	Subs. Metal (Me)	Si/Me ratio	Support	No. of Layers	Pervapor. Flux at 300 K (g/m ² ·h)	
					<i>o</i> -Xylene	TIPB
M1	Al	600	Stainless steel	3	57	5
M2	Al	600	Stainless steel	3	6	5
M3	Al	600	α-Al ₂ O ₃	3	2	< 1
M4	Al	600	α-Al ₂ O ₃	3	25	2.5
M5	B	100	Stainless steel	2	18	2.5
M6	B	100	Stainless steel	2	50	5

* NaOH concentrations in the synthesis gel for M2 and M3 were half of those used for M1 and M4.

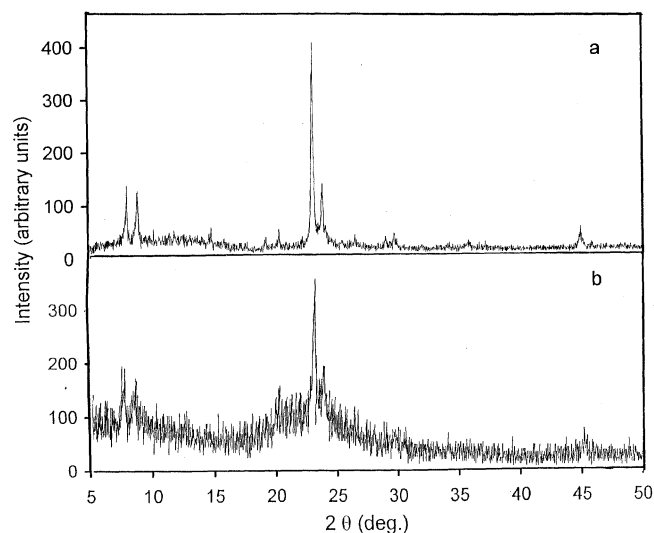


Figure 1. XRD spectra of powders collected when preparing.

(a) Al-ZSM-11 membrane M3 on an alumina support; (b) B-ZSM-11 membrane M5 on a stainless-steel support.

diameter. Slightly larger crystals ($1.5\text{--}2.5\ \mu\text{m}$) were observed on the surface of the B-ZSM-11 membrane (Figure 2b). The SEM cross section of the Al-ZSM-11 membrane (Figure 2c) indicates that the zeolite layer was $25\text{--}30\ \mu\text{m}$ thick. The stainless-steel-supported B-ZSM-11 membrane was difficult to break for SEM analysis of the cross section, but the zeolite layer appeared to be $20\text{--}25\ \mu\text{m}$ thick.

Pervaporation of alcohol/water mixtures

Table 2 shows separation performance at 333 K for aqueous feeds that contained 5 wt. % methanol or ethanol. The total fluxes were approximately twice as high for methanol/water as for ethanol/water for all membranes except M1. The separation selectivities were significantly higher for the ethanol/water mixtures. The selectivities for all Al-ZSM-11 membranes were similar; the methanol/water selectivities were less than 3, and the ethanol/water selectivities were less than 6. For the B-ZSM-11 membranes, however, methanol/water selectivities were 12 and 18, and ethanol/water selectivities were 24 and 42. The pervaporation measurements for 5 wt. % ethanol/water were repeated for membranes M2, M4, and M5 after three weeks. The fluxes and selectivities were reproducible within 10%, indicating that these membranes did not degrade due to repeated pervapo-

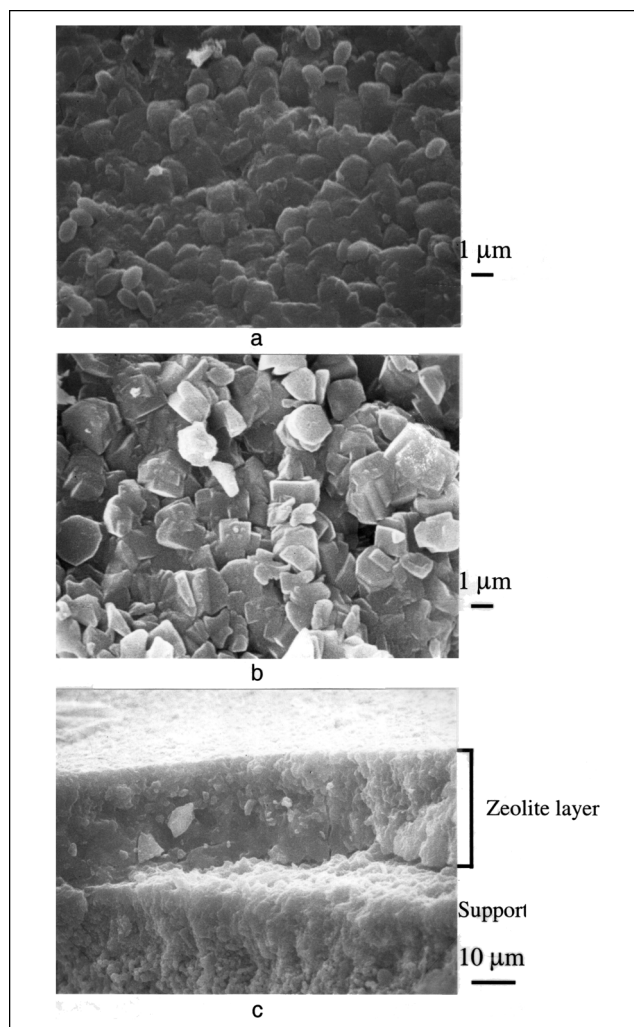


Figure 2. SEM micrographs.

(a) Surface of Al-ZSM-11 membrane M3 on an alumina support; (b) surface of B-ZSM-11 membrane M6 on a stainless-steel support; (c) cross section of Al-ZSM-11 membrane M3 on an alumina support.

ration measurements and calcinations. Since membrane M5 had the highest selectivities, it was used for more extensive studies.

Methanol/Water Separations. The fluxes of pure methanol, pure water, and 5 wt. % methanol/water solution through membrane M5 increased with temperature (Figure 3). The pure methanol fluxes were 2.5–3 times higher than the pure

Table 2. Pervaporation Measurements at 333 K

Memb.	5 wt. % Methanol/Water		5 wt. % Ethanol/Water	
	Total Flux ($\text{kg}/\text{m}^2 \cdot \text{h}$)	Selectivity	Total Flux ($\text{kg}/\text{m}^2 \cdot \text{h}$)	Selectivity
M1	2.5	1.7	1.8	2.3
M2	0.85	2.0	0.42	4.7
M3	0.34	2.9	0.21	5.4
M4	1.9	2.7	0.99	3.8
M5	1.7	18	0.93	42
M6	2.3	12	1.2	24

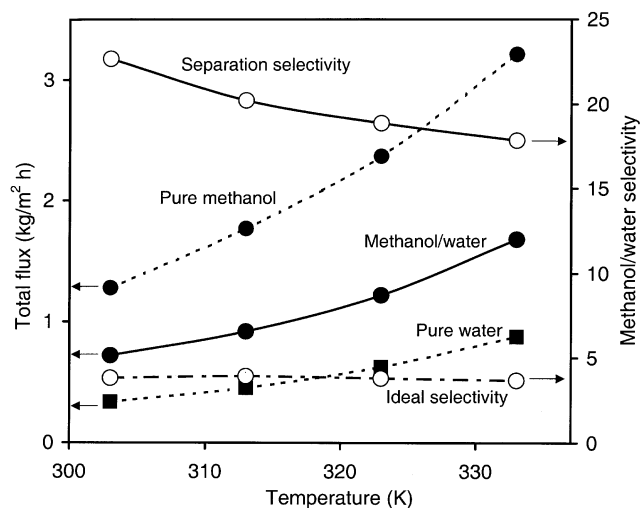


Figure 3. Total flux and methanol/water selectivity as a function of temperature for pervaporation of a 5 wt. % methanol aqueous solution through a B-ZSM-11 membrane (M5).

The fluxes of pure water and pure methanol and the ideal selectivity are also shown.

water fluxes, and the total fluxes of the binary mixture were between the pure component fluxes. The methanol/water separation selectivities were more than four times higher than the ideal selectivities, and the separation selectivity decreased with temperature. The maximum total flux was 1.7 kg/m²·h (at 333 K), and the maximum separation selectivity was 23 (at 303 K).

Figure 4 shows the total fluxes and methanol/water separation selectivities at 333 K as a function of the methanol feed concentration. The total flux increased and the separa-

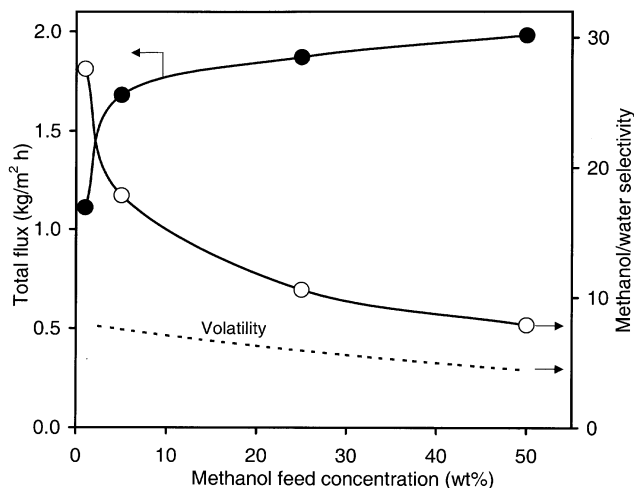


Figure 4. Total flux and methanol/water selectivity at 333 K as a function of the methanol feed concentration for pervaporation through a B-ZSM-11 membrane (M5).

The volatility for methanol/water is shown for comparison.

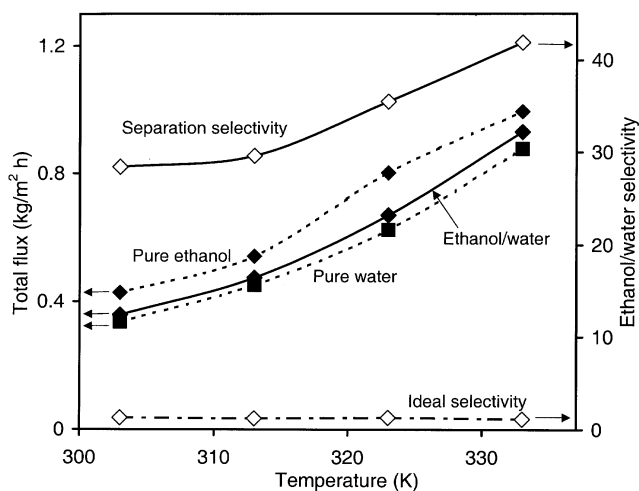


Figure 5. Total flux and ethano/water selectivity as a function of temperature for pervaporation of a 5 wt. % ethanol aqueous solution through a B-ZSM-11 membrane (M5).

The fluxes of pure water and pure ethanol, and the ideal selectivity are also shown.

tion selectivity decreased sharply as the methanol feed concentration increased from 1 wt. % to 5 wt. %. As the methanol concentrations increased further, the total flux increased more slowly. The methanol/water separation selectivities were higher than their volatilities. The highest separation selectivity of 28 was obtained for a feed concentration of 1 wt. %.

Ethanol/Water Separations. The fluxes of pure ethanol, pure water, and 5 wt. % ethanol/water solution through membrane M5 increased with temperature (Figure 5). The pure ethanol fluxes were a little higher than the pure water fluxes, and the total fluxes for the mixture were between them. The ethanol/water separation selectivities increased with temperature and were more than 20 times higher than the ideal selectivities. The maximum total flux was 0.93 kg/m²·h (at 333 K), and the maximum ethanol/water selectivity was 42 (at 333 K).

Figure 6 shows that the total flux for ethanol aqueous solutions through membrane M5 was essentially independent of ethanol feed concentration. The ethanol/water separation selectivities were larger than their volatilities, though the difference was small at high ethanol feed concentrations. The separation selectivity decreased from 97 to 5.1 as the ethanol feed concentration increased.

Propanol/Water Separations. The fluxes through membrane M5 of pure 1-propanol, 2-propanol, 5 wt. % 1-propanol/water, and 5 wt. % 2-propanol/water solutions all increased with temperature (Figure 7). The pure water fluxes were 3–7 times higher than the pure propanol fluxes. The total fluxes for the 1-propanol/water mixture were approximately 70% of those for the 2-propanol/water mixture. The 1-propanol/water separation selectivities were significantly higher than the 2-propanol/water separation selectivities. Both selectivities (Figure 7) increased with temperature and were higher than the ideal selectivities, which were much less

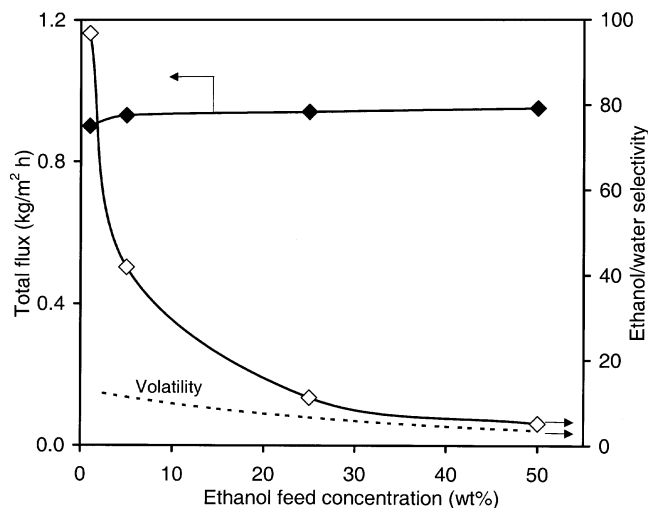


Figure 6. Total flux and ethanol/water selectivity at 333 K as a function of the ethanol feed concentration for pervaporation through a B-ZSM-11 membrane (M5).

The volatility for ethanol/water is shown for comparison.

than one. At 333 K, the 1-propanol/water separation selectivity was 25 with a total flux of 0.25 kg/m²·h, whereas the 2-propanol/water separation selectivity was 16 with a total flux of 0.31 kg/m²·h.

The fluxes and propanol/water selectivities at 333 K decreased with propanol feed concentration, as shown in Figure 8. Separation selectivities were higher for the 1-propanol solution than the 2-propanol solution, but total fluxes were lower. The 1-propanol/water separation selectivities were

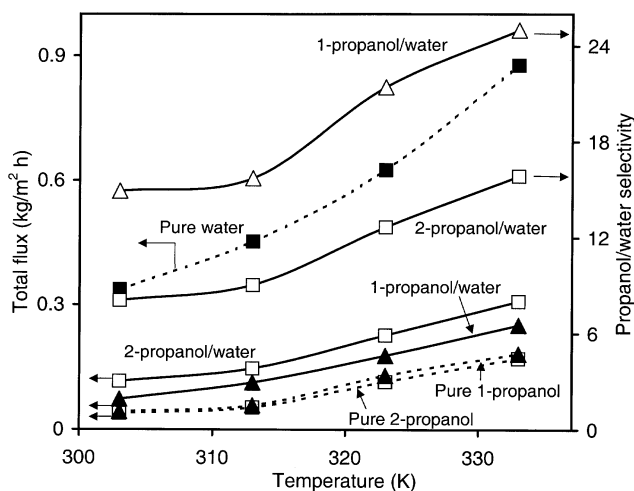


Figure 7. Total fluxes and 1-propanol/water and 2-propanol/water selectivities as a function of temperature for pervaporation of 5 wt. % 1- and 2-propanol aqueous solutions through a B-ZSM-11 membrane (M5).

The fluxes of pure water, pure 1-propanol, and pure 2-propanol are also shown.

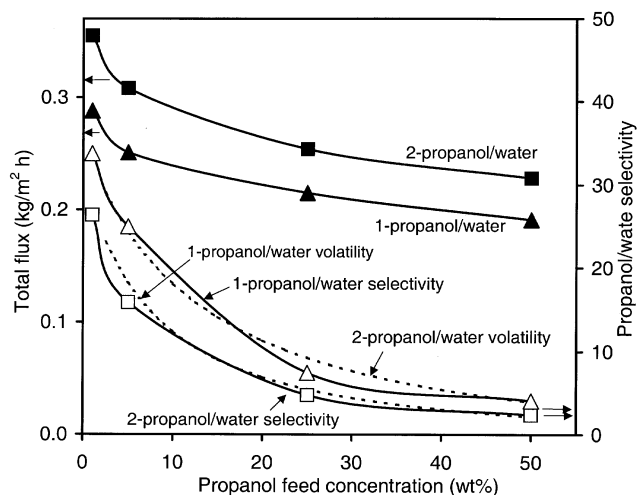


Figure 8. Total flux, and 1- and 2-propanol/water selectivities as a function of feed concentration for pervaporation through a B-ZSM-11 membrane (M5) at 333 K.

The volatilities for 1-propanol/water and 2-propanol/water are shown for comparison.

higher than their volatilities, whereas the 2-propanol/water selectivities were lower than their volatilities. The maximum 1-propanol/water and 2-propanol/water separation selectivities were 34 and 26, respectively, at 1 wt. % feed.

Discussion

Membrane quality and hydrophobicity

The kinetic diameter of *o*-xylene is 0.685 nm, and thus it diffused only through nonzeolite pores. Membranes M1 and M6 had higher *o*-xylene fluxes (50, 57 g/m²·h) than membranes M2, M3, and M5 (< 20 g/m²·h), indicating that these membranes had more or larger nonzeolite pores. Moreover, the *o*-xylene fluxes for membranes M1 and M6 were approximately 10 times the TIPB fluxes, which were 5 g/m²·h. If *o*-xylene and TIPB molecules diffuse at similar rates in the nonzeolite pores, then most of the nonzeolite pores had diameters less than 0.85 nm. The lower NaOH concentration in the Al-ZSM-11 synthesis gel increased the membrane qualities, as indicated by the lower *o*-xylene fluxes for membranes M2 and M3.

Membranes M4 and M5 had similar *o*-xylene and TIPB fluxes (Table 1), and thus they should have similar membrane qualities. Likewise, M1 and M6 should have similar membrane qualities. Indeed membranes M4 and M5 have similar total fluxes for methanol/water and ethanol/water mixtures. Likewise, membranes M1 and M6 have similar total fluxes for these mixtures. However, the B-ZSM-11 membranes (M5 and M6) had significantly higher methanol/water and ethanol/water separation selectivities than the Al-ZSM-11 membranes (M1 and M4). This may be because B-ZSM-11 membranes are more hydrophobic than Al-ZSM-11 membranes.

For MFI zeolites, the surface changes from hydrophobic (silicalite-1) to hydrophilic when Si is replaced by Al in the

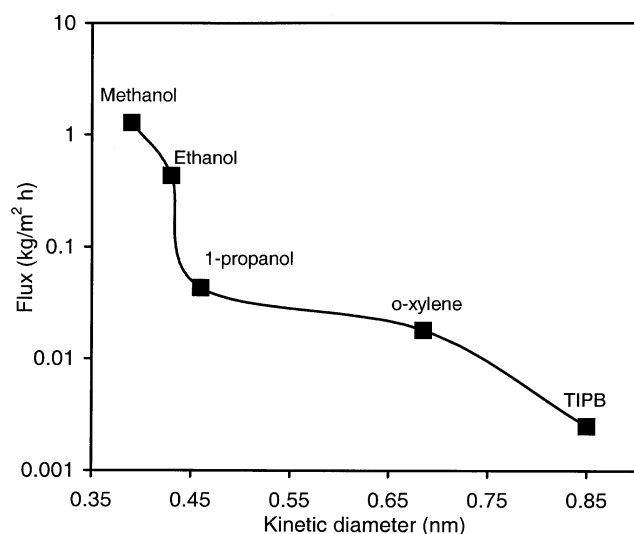


Figure 9. Pervaporation fluxes of pure components at 303 K (300 K for *o*-xylene and TIPB) as a function of kinetic diameter for a B-ZSM-11 membrane (M5).

framework. However, B-ZSM-5 membranes (Tuan et al., 2002) selectively permeated alcohols and ketones from aqueous solutions by pervaporation. The total fluxes were similar to those for a silicalite-1 membrane, but the organic/water selectivities were higher, indicating that B-ZSM-5 is also hydrophobic. By analogy, B-ZSM-11 is expected to be more hydrophobic than Al-ZSM-11.

Separation mechanism

The kinetic diameters of methanol, ethanol, and 1-propanol are 0.39, 0.43, and 0.46 nm, respectively, which are smaller than the MEL zeolite pores as measured by XRD (0.54×0.53 nm). The B-ZSM-11 membrane M5 was selective for *n*-C₄H₁₀ over *i*-C₄H₁₀ even at 473 K, indicating that the membrane was of reasonable quality. Thus, the alcohols are expected to permeate mainly through zeolite pores. The fluxes of pure alcohols through membrane M5 at 303 K decreased dramatically with carbon number (Figure 9) because larger alcohols absorb more strongly (Sano et al., 1994) and diffuse slower.

The alcohol/water separation selectivities do not correlate with the volatilities; for example, 2-propanol is more volatile than 1-propanol, but its separation selectivities are lower. Instead, the alcohol/water separation selectivities are significantly higher than their ideal selectivities (Figures 3, 5, and 7), indicating that preferential adsorption of alcohols is responsible for separation.

The driving force for pervaporation is the difference in the feed and permeate surface concentrations. At relative low alcohol concentrations, for example, 1 wt. % alcohol does not saturate the feed side of the membrane, and the alcohol fluxes are low (Table 3). Alcohol adsorption increases with feed concentration, and thus the alcohol flux increases. Higher alcohol coverage blocks water adsorption and thus decreases water flux. The total flux for methanol/water increases with

Table 3. Pervaporation Measurements at 333 K

Aqueous Solution	Alcohol Flux (kg/m ² ·h)			
	1 wt. %	5 wt. %	25 wt. %	50 wt. %
Methanol	0.24	0.81	1.5	1.8
Ethanol	0.42	0.64	0.74	0.79
1-Propanol	0.073	0.14	0.15	0.15
2-Propanol	0.072	0.13	0.14	0.14

feed concentration (Figure 4) because methanol diffuses faster than water. In contrast, the total fluxes for 1-propanol and 2-propanol aqueous solutions decrease with feed concentration because they block water and they diffuse slower than water (Figure 7). The total flux for the ethanol aqueous solution was essentially independent of feed concentration because the ethanol and water diffusion rates were similar. Alcohol separation selectivities decreased dramatically as the alcohol feed concentration increased (Figures 4, 6, and 8) because as the feed concentration increased, the alcohol coverage on the feed side did not increase proportionally, and thus the alcohol fluxes did not increase as much as the feed concentration (Table 3). Note that the larger alcohols saturate the surface at lower concentration (Table 3) since they adsorb more strongly. For example, as the alcohol concentration increased from 5 to 25 wt. % the methanol flux almost doubled but the propanol fluxes were almost unchanged.

Figure 10 presents water fluxes for the aqueous solutions and for pure water at 333 K through the B-ZSM-11 membrane M5. For the linear alcohols, the water flux decreases as the molecular size increases. Thus, the larger linear alcohols more effectively block water permeation. The alcohol/water separation selectivities might be expected to increase the same way if they were only controlled by the preferential adsorption of alcohols. However, the alcohol diffusion rates decrease with increasing size. Thus, as shown in Figure 10, at 333 K, the highest separation selectivity was obtained for

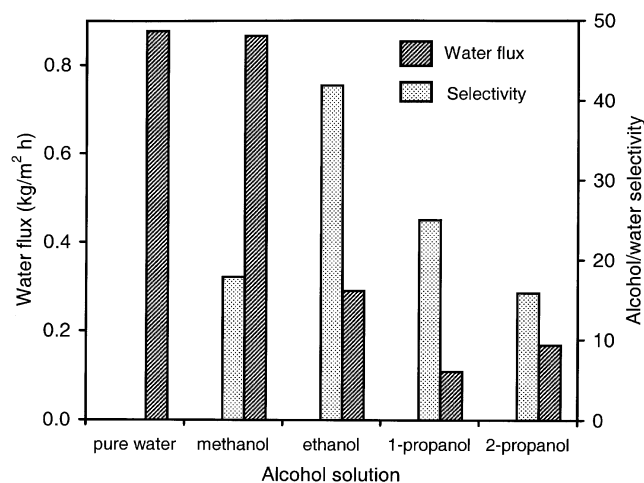


Figure 10. Water flux and alcohol/water selectivities at 333 K for pervaporation of 5 wt. % alcohol/water solutions through a B-ZSM-11 membrane (M5).

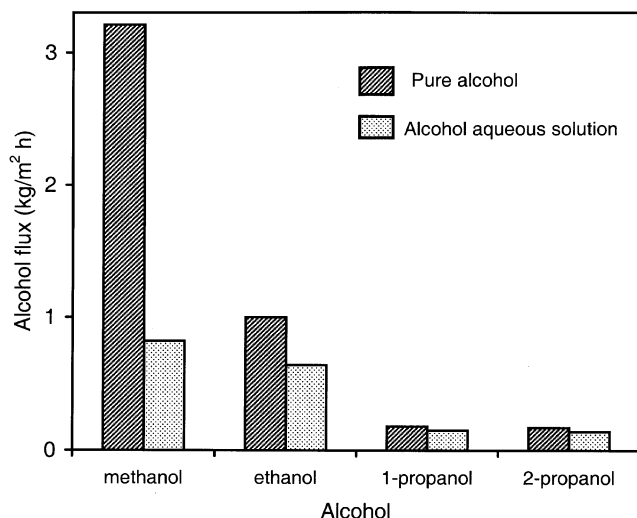


Figure 11. Pervaporation flux of alcohols through a B-ZSM-11 membrane (M5) at 333 K.

The fluxes are for pure alcohol and for 5 wt. % alcohol in water.

ethanol/water. The ethanol/water selectivity was higher than the methanol/water selectivity because ethanol decreased water flux to one-third of its pure component value, whereas methanol did not inhibit water permeation (Figure 10). Thus, the ethanol/water selectivity was higher even though ethanol diffused slower than methanol. The other alcohols strongly inhibited water permeation (Figure 10), but they diffused slower than ethanol (Figure 11), and the diffusion rate dominated, so their separation selectivities were lower than the ethanol/water selectivity.

The water flux for 1-propanol/water was lower than for 2-propanol/water (Figure 10), indicating that 1-propanol absorbed more strongly than 2-propanol. Moreover, 1-propanol is smaller than 2-propanol, and thus diffuses faster (Figure 11). Therefore, separation selectivities for 1-propanol/water were higher than for 2-propanol/water. Similarly, Sano et al.

(1994) observed lower total flux, but higher separation selectivity for 1-propanol/water than 2-propanol/water for a silicalite-1 membrane.

Comparison to MFI membranes

Table 4 compares pervaporation total fluxes and separation selectivities for alcohol/water solutions for zeolite membranes reported in the literature. The B-ZSM-5 membrane (Tuan et al., 2000, 2002) was prepared by a similar procedure to that used for the B-ZSM-11 membrane. All the other studies used silicalite-1 membranes.

Sano et al. (1994) indicated that their silicalite-1 membranes had nonzeolite pores larger than 1 nm, and molecules permeated mainly through nonzeolite pores. Their separation selectivities increased with carbon number because larger alcohols absorbed more strongly and thus more effectively blocked water. Our B-ZSM-11 membrane behaved differently because it has fewer nonzeolite pores larger than 0.85 nm, as indicated by its low TIPB flux and relative high $n\text{-C}_4\text{H}_{10}/i\text{-C}_4\text{H}_{10}$ ideal selectivities.

Another difference from the silicalite-1 membranes of Sano et al. (1994) is the effect of temperature on separation selectivities. For the B-ZSM-11 membrane, only the methanol/water separation selectivity decreased with temperature, and the other separation selectivities increased. In contrast, Sano et al. (1994) observed that all alcohol/water separation selectivities decreased with temperature. The difference was because their separation selectivities were mainly based on preferential adsorption of alcohols. At higher temperature, alcohols adsorbed less strongly and selectivities decreased. For the B-ZSM-11 membrane, separation selectivity was controlled by both diffusion rate and preferential adsorption. As the temperature increased, the diffusion rate increased, but adsorption coverage decreased. Apparently, the diffusion rate dominated in the B-ZSM-11 membrane for all the alcohols except methanol.

The silicalite-1 membrane of Nomura et al. (1998) showed similar total fluxes and ethanol/water separation selectivities as those reported by Sano et al. (1994), since both mem-

Table 4. Pervaporation Results for Alcohol/Water Mixtures in the Literature

Solution	Membrane	Feed Conc.(wt. %)	Temp. (K)	Total Flux (kg/m ² ·h)	Sep. Sel.	Reference
Methanol/water	Silicalite-1	1.8	333	1.6	17	Sano et al. (1994)
	Silicalite-1	3.5	305	0.75	7.5	Liu et al. (1996)
	B-ZSM-5	5	333	0.44	78	Tuan et al. (2002)
	B-ZSM-11	5	303	0.72	23	This work
	B-ZSM-11	5	333	1.7	18	This work
Ethanol/water	Silicalite-1	2.5	333	0.72	50	Sano et al. (1994)
	Silicalite-1	9.7	305	0.10	12	Liu et al. (1996)
	Silicalite-1	4.65	303	0.60	64	Nomura et al. (1998)
	B-ZSM-5	5	333	0.09	9.4	Tuan et al. (2002)
	B-ZSM-11	5	303	0.36	29	This work
	B-ZSM-11	5	333	0.93	42	This work
1-propanol/water	Silicalite-1	3.3	333	0.16	76	Sano et al. (1994)
	B-ZSM-5	5	333	0.07	7.8	Tuan et al. (2002)
	B-ZSM-11	5	333	0.25	25	This work
2-propanol/water	Silicalite-1	3.3	333	0.22	36	Sano et al. (1994)
	B-ZSM-5	5	333	0.07	7.0	Tuan et al. (2002)
	B-ZSM-11	5	333	0.31	16	This work

branes were prepared by similar procedures and had similar thicknesses. The silicalite-1 membrane (10 μm) used by Liu et al. (1996) had a $n\text{-C}_4\text{H}_{10}/i\text{-C}_4\text{H}_{10}$ selectivity of 3 at 298 K. Their membrane apparently contained nonzeolite pores, that were larger than the MFI pores, since higher $n\text{-C}_4\text{H}_{10}/i\text{-C}_4\text{H}_{10}$ permselectivities have been reported for the same type membrane (Vroon et al., 1996; Bakker et al. 1996; Moueddeb et al., 1998). Thus the methanol/water selectivity was low. The ethanol/water separation selectivity observed by Liu et al. (1996) was only one-sixth of those reported by Sano et al. (1994) and Nomura et al. (1998), which is probably due to the differences in number or size of nonzeolite pores.

The fluxes through the B-ZSM-11 membrane were approximately three times the fluxes through the B-ZSM-5 membrane of Tuan et al. (2002) for some alcohol/water mixtures. For ethanol/water, the flux was more than nine times higher. Both membranes had two layers prepared by similar procedures and the same Si/B ratios, so they were expected to have similar hydrophobicities. However, for the B-ZSM-5 membrane, the highest separation selectivities (> 70) were observed for methanol/water, and alcohol/water separation selectivity decreased with increasing carbon number. The B-ZSM-5 membrane had fewer nonzeolite pores than the B-ZSM-11 membrane, since it had a TIPB flux less than 0.1 $\text{g}/\text{m}^2\cdot\text{h}$, which was only one-twentieth of the B-ZSM-11 membrane. Methanol did not block water in either membrane, and diffusion rates dominated the methanol/water separation selectivities. Thus the higher-quality B-ZSM-5 membrane had higher selectivities. For the larger alcohols, however, preferentially adsorption played a significant role for both membranes.

Summary

Alcohols ($\text{C}_1\text{--C}_3$) were preferentially separated from aqueous solutions through B-ZSM-11 zeolite membranes. At 333 K, for 5 wt. % alcohol feed aqueous solutions, the total fluxes decreased from 1.7 $\text{kg}/\text{m}^2\cdot\text{h}$ to 0.25 $\text{kg}/\text{m}^2\cdot\text{h}$ as the carbon number increased. All separation selectivities increased with decreasing alcohol feed concentrations. In an alcohol concentration range of 1 to 50 wt. % at 333 K, the separation selectivities for the linear alcohols were higher than expected for vapor/liquid equilibrium separations. At 333 K, the highest separation selectivities for 1 wt. % alcohol solutions were 28, 97, 34, and 26 for the $\text{C}_1\text{--C}_3$ alcohols. The alcohol/water separation selectivities were controlled by both preferential adsorption of alcohols and differences in diffusion rates.

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