

Pervaporation and Vapor Permeation Properties of Commercialized T-type Zeolite Membranes

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T-type Zeolite membranes were grown hydrothermally on the surface of a porous cylindrical substrate of mullite and were characterized by X-ray diffraction, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The surface of the mullite support were completely covered with T-type zeolite crystals and the thickness of the membrane were about 20 μm judging from the cross sectional view of SEM observation. EPMA analysis revealed that the cross section of the membrane consisted of three layers—the zeolite layer, the intermediate layer and the mullite support. The membranes displayed excellent water-permeable performance in pervaporation (PV) and vapor permeation (VP) for water/organic liquid mixtures. With an increase in temperature, both the permeation flux Q and the separation factor α increased, and the membrane performance was the same for PV as for VP at around saturated temperature. In PV of organic liquid mixtures with 10 wt% water at 100 $^{\circ}\text{C}$, Q values were 2.0, 2.0, and 2.5 $\text{kgm}^{-2}\text{h}^{-1}$ and α values were 3000, >10000 and >10000 for the water/ethanol, *i*-propanol and /tetrahydrofuran mixtures, respectively.

Key words: Pervaporation, Vapor permeation, Zeolite membrane, T-type zeolite, Dehydration

1. INTRODUCTION

As pervaporation (PV) is an attractive means for the dehydration of water/organic mixtures, membranes for PV of these liquid mixtures have been widely investigated [1-3]. Inorganic membranes are generally superior to polymeric membranes in thermal, mechanical and chemical stability. Zeolite NaA membranes and modules on a large commercial scale, developed by our group, have been used for the dehydration of organic liquids [4-9]. Application of the zeolite NaA membranes, however, is limited mainly because of their insufficient acid resistance. Recently, Kita et al. [10] reported that T-type zeolite membrane was stable in acid solution although the separation factor of the membrane for water/alcohol mixtures was slightly smaller than that of zeolite NaA membrane on a laboratory scale. In this paper, the characterization of commercialized T-type zeolite membranes and their PV and vapor

permeation (VP) properties for water/organic liquid mixtures are reported.

2. EXPERIMENTAL

2.1 Membrane Preparation

T-type zeolite membranes were synthesized hydrothermally on porous mullite tubes (Nikkato). The materials used for the synthesis were colloidal silica (Aldrich), sodium aluminate (Wako). The porous tubes with dimensions of 12 mm o.d., 9 mm i.d. and 800 mm length were used as the substrates of the zeolite membranes. They had an average pore size of 1 μm and a porosity of about 40 %.

An aluminate solution, which was prepared by dissolving sodium hydroxide, potassium hydroxide and sodium aluminate in distilled water, was added to colloidal silica and the mixture was stirred for 45 min to produce a homogeneous gel. The molar composition of the resulting gel was $\text{SiO}_2/\text{Al}_2\text{O}_3 = 112$, $\text{Na}^+(\text{Na}^+ + \text{K}^+) = 0.77$, $\text{OH}^-/\text{SiO}_2 = 0.77$

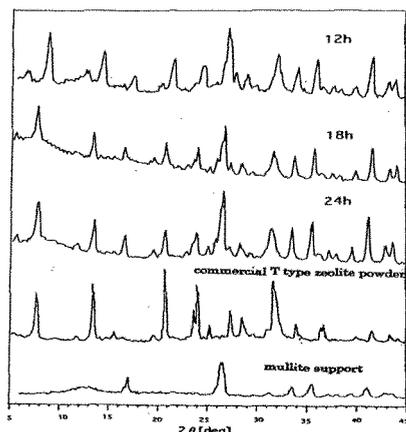


Fig.1 X-ray diffraction patterns of T-type zeolite membrane prepared on mullite support at varying crystallization time, commercial T-type zeolite powder and mullite support.

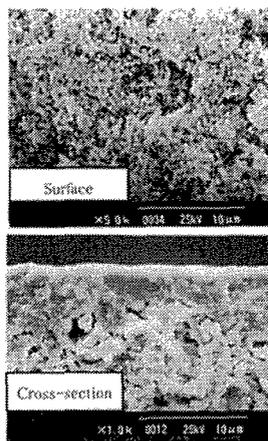


Fig.2 SEM micrographs of the surface and cross-section of the T-type zeolite membrane prepared at 100 °C for 24 hours.

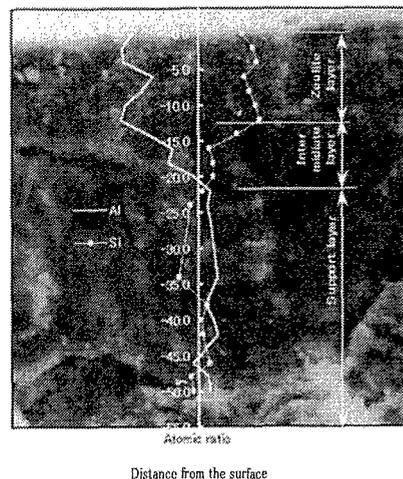


Fig.3 Distribution of Al and Si in cross-section of T-type zeolite membrane by EPMA analysis.

and $H_2O/(Na^+ + K^+) = 20.75$. After formation of the gel, the reaction mixture was stored at ambient temperature until changing from cloudy solution to clear one. Several porous substrates coated by the seed crystals were placed in the gel. After hydrothermal treatment at 100 °C for 24 h, the substrates were washed with water and dried at room temperature.

The formation of the zeolite membranes was confirmed by using X-ray diffraction (XRD) with $Cu-K\alpha$ radiation. The surface morphologies of the membrane were observed by scanning electron microscopy (SEM). The compositions of the specimen cross section were analyzed by electron probe microanalysis (EPMA) with wavelength dispersive spectrometer (WDS). Cross sections of the membranes were obtained by microcutting of specimens.

2.2 PV and VP experiments

PV and VP experiments were carried out using the apparatus described elsewhere [4–10]. The effective membrane area, which was sealed in a stainless-steel module set in a thermostated air bath, was 289 cm² (ca. 800 mm in effective length). In PV experiments, liquid mixtures were preheated to a constant temperature and were then fed by a liquid pump from a liquid reservoir to the outer side of the membrane tube in the module at 80 cm s⁻¹. In VP experiments at 95–150 °C, the feed liquid was vaporized by a superheater and then fed to the outer side of the membrane tube at a flow velocity of 8–12.5 ms⁻¹. The feed vapor pressure was controlled in the range of 0.1–0.5 MPa at the outlet of the feed vapor.

The inside of the membrane tube was evacuated through a vacuum line. The permeate pressure was measured inside the module and was maintained below 13.3 Pa unless otherwise stated. The permeated vapor was compressed by mechanical booster pump to get the condensation of the vapor. The membrane performance was evaluated by permeation flux (Q in kg m⁻² h⁻¹) and a separation factor (α). The separation factor was defined by $\alpha = (y_w/y_o)/(x_w/x_o)$, where y_w/y_o is the weight ratio of water to organic liquid in the permeate and x_w/x_o is that of water to organic liquid in the feed. Composition analysis was performed with a gas chromatography.

3. RESULTS AND DISCUSSION

3.1 T-type zeolite membrane

Figure 1 shows XRD patterns of mullite support, the zeolite membrane prepared on the mullite support at varying crystallization time and commercial T-type zeolite powder. The intensities of the diffraction peaks corresponding to T-type zeolite increased with an increase in the crystallization time. The SEM photographs of the surface and cross-section of the zeolite membrane prepared for crystallization time of 24 h are shown in Fig. 2. The surface of the mullite support is completely covered with T-type zeolite crystals. These crystals tend to be very closely bound together with little space between them.

It was found by the cross sectional SEM observation that the thickness of the membranes was about 20 μm. The atomic compositions of Al and Si on the cross section were obtained by EPMA analysis, as shown in

Fig. 3. EPMA analysis reveals that the zeolite membranes consist of three layers. The outer layer is a zeolite layer and the inner is the support, since both compositions agree with those of commercial T-type zeolite powder and mullite support, respectively. The layer between the zeolite layer and support has the intermediate composition.

Table 1 PV and VP performance of the T-type zeolite membranes toward water/organic liquid systems

Feed solution(A/B) (wt% of A)	Temp. (K)	Separation factor (A/B)	Flux (kgm ⁻² h ⁻¹)
Water/Ethanol(10)	323	2100	0.50
	348	2100	1.18
	373	3000	2.0 (VP)
Water/i-Propanol(10)	348	10000	1.70
	373	10000	2.0 (VP)
Water/THF(10)	348	10000	1.80
	373	10000	2.5

3.2 Permeation properties

Table 1 shows PV and VP properties of the zeolite membrane for water/organic liquid mixtures. The T-type zeolite membranes were highly water-permeable for these organic liquids and displayed extremely high permeation fluxes and separation factors. Even in the case of the water/tetrahydrofuran, where most of the polymeric membranes swell well, large flux and high separation factor were also observed. Figure 4 shows the p/p_s dependence of q_w and α in the VP of water/EtOH and water/IPA mixtures at 130°C for $x_w = 10$ wt%. Where p is the measuring vapor pressure and p_s is the saturated pressure calculated using the feed vapor composition x and the temperature t . The degree of superheat Δt is defined by the difference $(t - t_s)$ between the feed temperature t and the saturated temperature t_s .

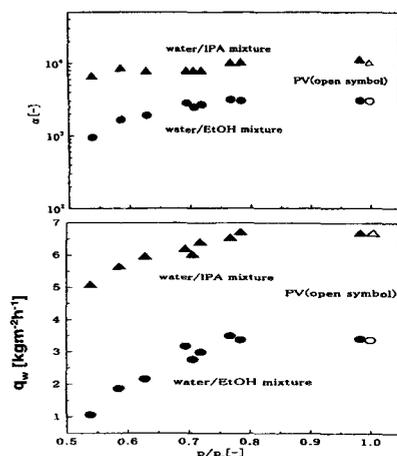


Fig.4 The degree of superheat for a feed vapor temperature (p/p_s) dependence of q_w and α in VP of water/EtOH and water/IPA mixture of $x_w = 10$ wt% at 130 °C through T-type zeolite membrane.

calculated using the feed vapor composition x and measuring pressure p . With p/p_s ranging from 1 to around 0.77, q_w hardly changed. In the range of less than $p/p_s = 0.77$, q_w decreased significantly with a decrease of p/p_s . When the degree of superheat for vapor temperature in VP was more than $p/p_s = 0.77$ at 95–150 °C, VP performance of the zeolite membrane was the same as PV one. The VP performance at the degree of superheat less than $p/p_s = 0.77$ depended upon feed pressure.

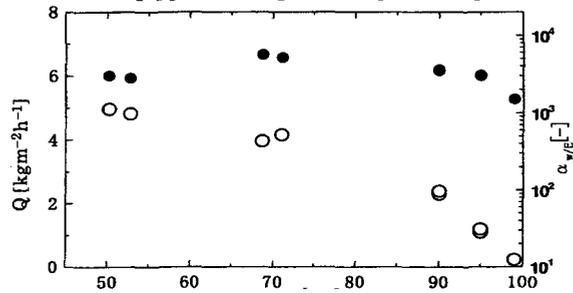


Fig.5 Feed composition dependence of Q and α in PV of water/EtOH for T-type zeolite membrane at 110 °C.

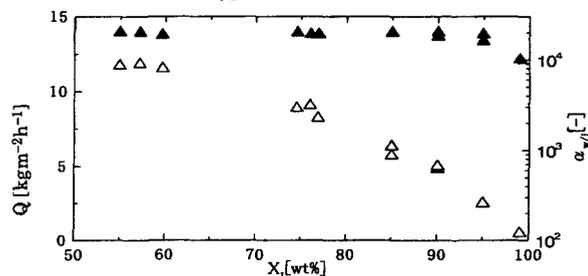


Fig.6 Feed composition dependence of Q and α in PV of water/IPA for T-type zeolite membrane at 110 °C.

Figures 5 and 6 show the feed composition dependence of the permeation flux and separation factor in PV of water/*i*-propanol (IPA) and water/ethanol (EtOH) mixtures, respectively. In the entire feed range, the total permeation flux Q was substantially equal to the water flux q_w , and the EtOH and IPA fluxes q_E and q_I were below 9×10^{-3} and 4×10^{-3} kgm⁻²h⁻¹. With an increase in x_w , Q increased initially linearly and then gradually and finally saturated. The other hand, with an increase in x_w , α increased initially and reached a constant value. The temperature dependence of the water flux through the zeolite membrane in water/EtOH and water/IPA mixtures is shown in Fig. 7. From these Arrhenius plots, the apparent activation energies ΔE_{ap} of water permeation were calculated to be 26 kJmol⁻¹ and 28 kJmol⁻¹ for water/EtOH and water/IPA mixtures at a feed of 10 wt% water, respectively.

Figure 8 shows that both q_w and α at $x_w = 10$ wt% were independent of the downstream pressure in the range up to 2 kPa.

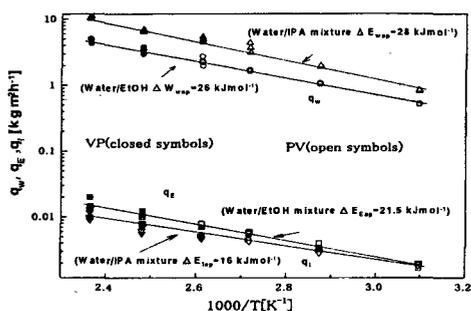


Fig.7 Temperature dependence of q_w , q_g , q_l and α in PV(open symbols) and VP(close symbols) of water/EtOH and water/IPA mixtures of $x_w=10$ wt%, respectively, through T-type zeolite membrane.

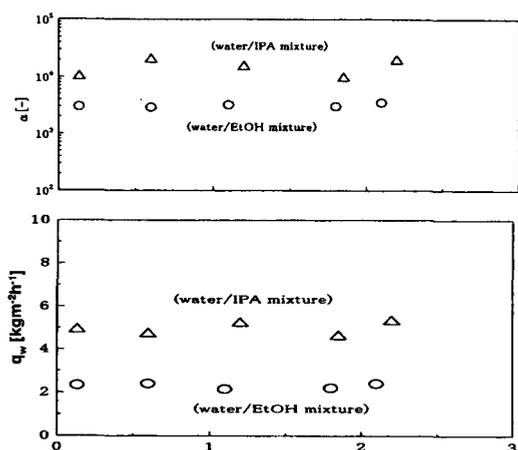


Fig.8 Downstream pressure dependence of q_w and α at 10 wt% in PV of water/EtOH and water/IPA mixtures for T-type zeolite membrane.

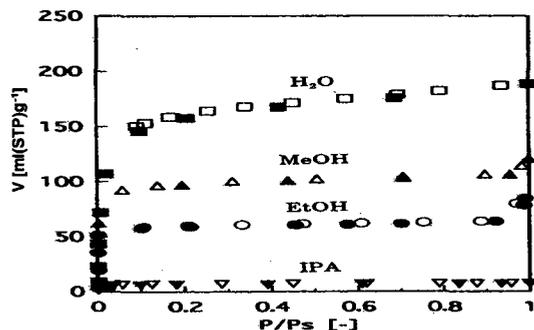


Fig.9 Adsorption isotherms of water, methanol (MeOH), ethanol (EtOH) and i-propanol (IPA) for T-type zeolite powder at 25 °C. The open and closed symbols refer to adsorption and desorption, respectively.

As shown in Fig. 9, the adsorption amounts of vapors on T-type zeolite crystal powder were in the order, water > MeOH > EtOH > IPA. At 25 °C, the adsorption of water vapor was only 3.2 and 25 times larger than those of EtOH and IPA, respectively. The separation factors of PV and VP for water/EtOH and water/IPA mixtures were as high as 2000 and 10000 at $x_w = 10$ wt%, respectively. This suggests that the adsorption of alcohol is almost completely inhibited by the presence of water because of the competitive preferential adsorption and the blocking of

alcohol molecules from entering the pores.

4. CONCLUSION

(1) T-type zeolite membranes were prepared hydrothermally on the surface of porous mullite tubes, which were seeded with T-type zeolite crystals, using a gel with the composition $\text{SiO}_2/\text{Al}_2\text{O}_3=112$, $\text{Na}^+(\text{Na}^+ + \text{K}^+)=0.77$, $\text{OH}^-/\text{SiO}_2=0.77$ and $\text{H}_2\text{O}/(\text{Na}^+ + \text{K}^+)=20.75$.

(2) The membrane consists of three layers. The outer layer is a zeolite layer and the inner is the mullite support. The layer between the zeolite layer and support has the intermediate composition.

(3) The membranes displayed the excellent water-permselective performance in PV and VP for water/organic liquid mixtures in the entire feed range. With an increase in temperature, both Q and α increased, and the membrane performance was the same for PV as for VP at around saturated temperature. In PV of organic liquid mixtures with 10 wt% water at 100 °C, Q values were 2.0, 2.0, and 2.5 $\text{kgm}^{-2}\text{h}^{-1}$ and α values were 3000, >10000, and >10000 for the water/EtOH, /IPA and /tetrahydrofuran mixtures, respectively.

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