Transport phenomena through zeolite NaA and T-type membranes

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Transport phenomena of alcohol/water mixture by pervaporation (PV) through zeolite NaA and T-type membranes were studied. Average Kelvin diameters, which were defined as the diameters at a dimensionless flux of 50%, were 1.4nm for a NaA membrane and 0.8 nm for a T-type membrane, respectively. Both of the NaA membrane and the T-type membrane were highly water selective adsorption for water/alcohol mixtures. The PV membrane performance is dependent on the type of alcohol. In the polar solvent (MeOH and EtOH), NaA membrane performance was higher than T-type membrane performance. In water/IPA mixture, the difference was smaller between the performance of NaA and T-type membrane. In spite of the type of alcohol, the water permeability K_i of the NaA membrane was constant (ca. 0.13) using partial vapor pressure difference as the driving force through the membrane. The water permeability K_i of the T-type membrane was respectively constant value of every alcohol when partial vapor pressure of feed side is over 30 kPa. Consideration of surface diffusion flow suggests that transport phenomena of the NaA membrane are mainly caused by the adsorption to the grain boundary clearance, while transport phenomena of the T-type membrane are caused by the adsorption to both of grain boundary clearance and zeolite pore.

Key words: Pervaporation, NaA zeolite membrane, T-type zeolite membrane, Dehydration, Transport phenomena

1. INTRODUCTION

Pervaporation (PV) is an attractive means as an effective and energy-efficient technique for the dehydration of water/organic mixtures [1]. Zeolite membranes offered significant potential for PV agent with high separation factor and permeation flux together with high chemical and thermal stability. In order to purify isopropanol (IPA) from cleaning process in industries such as precision machinery and electronics, and to dehydrate ethanol (EtOH) used in food industry, PV equipment using NaA-type zeolite membranes has been used practically [2]. The application of T-type zeolite membrane to liquid-phase reversible reactions is examined with the purpose of the improvement in the conversion with reaction [3].

Recently, the transport mechanism through a silicalite membrane was discussed using the adsorption-diffusion model [4], which is based on the solution-diffusion model for polymeric membranes. The silicalite membrane was hydrophobic and showed high alcohol selectivity, while both zeolite membranes of NaA and T-type were hydrophilic and showed extremely high water selectivity. Therefore, the PV transport phenomena of the both hydrophilic zeolite membranes seem to be different from those through the silicalite membrane.

The reports on the adsorption character of zeolite membranes have apparently not been published, though the adsorption character for each type of the zeolite powder has mainly been reported.

In this paper, the grain boundary clearance for each of NaA zeolite membranes and T-type zeolite membranes was measured using nanopermporometry [5,6]. The adsorption character for each of NaA membranes and T-type membranes was measured by the batch method using the alcohol/water mixtures. PV experiments were performed with water/alcohol mixtures at various temperatures and a wide range of concentration to study the transport phenomena of the NaA membrane and the T-type membrane.

2. EXPERIMENTAL

2.1 Preparation of NaA and T type zeolite membranes

NaA and T-type zeolite membranes were grown hydrothermally on the surface of porous cylindrical mullite tubes (12mm outer diameter, 1.5mm thickness, 1.0 μ m average pore size, 40% porosity). The details of preparation have been discussed elsewhere [7,8].

The molar compositions of the starting gel were $Al_2O_3:SiO_2:Na_2O:H_2O=1:2:2:120$ for NaA membrane and $Al_2O_3:SiO_2:(Na_2O+K_2O):H_2O=1:54:20.79:863$ for T-type membrane, respectively. Hydrothermal synthesis of NaA membrane was made at 373 K for 3.5 hours and T-type membrane was synthesized at 373 k for 24 hours.
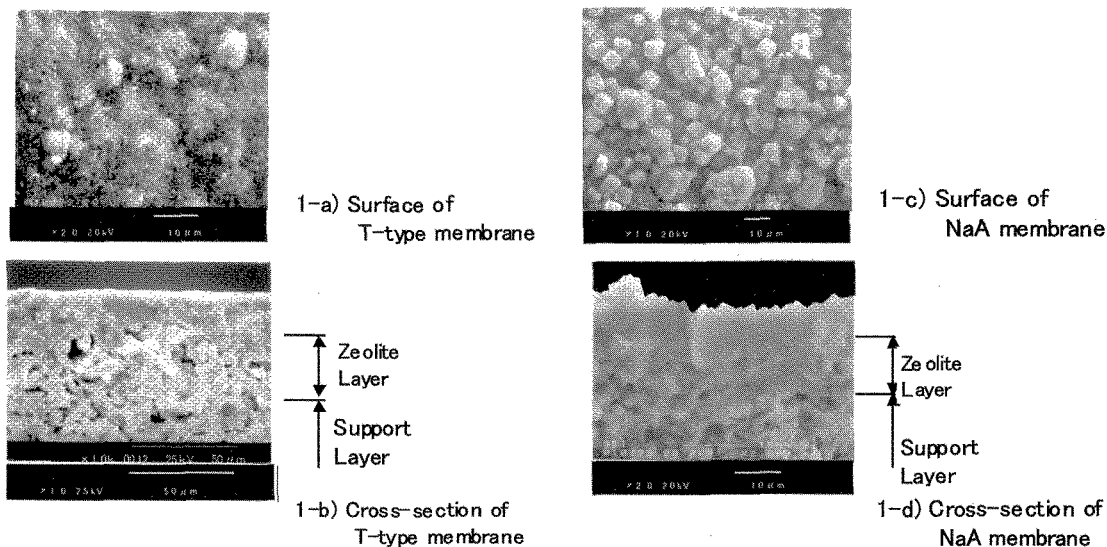
1-a) Surface of
T-type membrane

1-c) Surface of
NaA membrane

Zeolite
Layer

Support
Layer

1-b) Cross-section of
T-type membrane

Zeolite
Layer

Support
Layer

1-d) Cross-section of
NaA membrane

Fig1. SEM image of the zeolite membranes

Figure 1 shows the SEM microphotographs of these zeolite membranes. The surface of the mullite support is completely covered with each zeolite crystal, respectively. These crystals tend to be very closely bound together with little space between them. The thickness of the NaA membrane was about 10μm and the NaA crystals are arranged randomly, while that of T-type membrane was about 20μm and the T-type crystals seem to be orientated a little.

2.2 Nanopermporometry characterization of zeolite membranes

Grain boundary clearance of the zeolite membranes was measured using nanopermporometry (name of trade "Nanopermporometer", SEIKA), the basic principle of which lies in capillary condensation of water vapor in the fine pores at a given humidity and the blocking of non-condensable gas permeation through the condensed pores [5,6]. Nitrogen was used as a non-condensable gas, and the liquid used as a condensable vapor was water. Initially, permeation flux of membrane was measured with dry nitrogen at the measurement temperature. The vapor pressure was then increased gradually in a stepwise manner to a specific partial pressure, until nitrogen permeation was blocked by capillary condensation.

The zeolite membranes were fired in the vacuum of 473K to remove any adsorbates, and then, they were set in the equipment. For the calculation of Kelvin diameter based on Eq. (1), complete wetting, i.e. contact angle θ=0, was assumed.

$$RTln(p/p_{sat}) = -\nu\, 2\, \sigma \cos\theta\, /r_p \qquad (1)$$

Where p is water vapor pressure in the feed nitrogen gas and p_{sat} is the saturated vapor pressure, σ is the surface tension between water and nitrogen, v is the molar volume of water, and r_p is the capillary radius.

2.3 Adsorption measurement and PV experiment

Evaluation of water adsorption to zeolite powder and membrane was carried out using the batch method.

Every sample was fired in the vacuum of 473 K to remove any adsorbates, and then, the sample was placed in the sample chamber with water/alcohol mixture. The sample chamber was well shaken in a thermostated water bath. Adsorption was carried out until the equilibrium was reached. The equilibrium time was found by trial and error method. The adsorption period was at least 20h. After reaching the equilibrium, the water concentration in the sample chamber was measured by gas chromatography.

PV experiments with effective membrane area 36.6cm² (ca. 9.7cm in effective length) were carried out using the apparatus described elsewhere [9-12]. The membrane performance was evaluated by permeation flux (Q in $kgm^{-2}h^{-1}$) and a separation factor (α). The separation factor was defined by $\alpha=(y_w/y_0)/(x_w/x_0)$, where y_w/y_0 is the weight ratio of water to organic liquid in the permeate and x_w/x_0 is that of water to organic liquid in the feed. Composition analysis was performed with a gas chromatography.

3. RESULTS AND DISCUSSION

3.1 Nanopermporometry characterization of zeolite membranes

The permeation flux of nitrogen normalized with that of dry nitrogen is shown in Fig. 2 as a function of Kelvin diameter calculated by the Kelvin equation (1) without correction of the adsorption thickness of water vapor. It should be noted that the Kelvin equation loses physical meaning for pore diameters of less than 2nm. Though the present method cannot accurately evaluate the nanopermporometry characterization of zeolite membranes, it is an effective method for the comparison
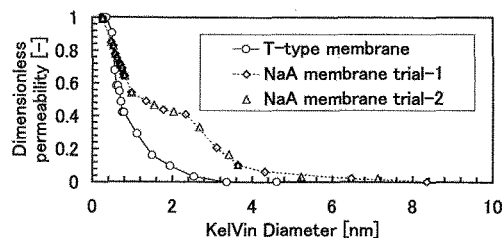

Fig.2 Dimensionless flux of nitrogen of zeolite membranes as function on Kelvin diameter

of the grain boundary clearance distribution of each membrane.

Average Kelvin diameters, which were defined as the diameters at a dimensionless flux of 50%, of NaA membrane and T-type membrane were determined to be 1.4 nm and 0.8 nm, respectively. Due to the blocking effect of nitrogen permeation by condensed water, no nitrogen permeation was observed that p/p_s was larger than 0.75 for the NaA membrane and 0.61 for the T-type membrane, respectively. These results indicate that these zeolite membranes are composed of grain boundary and grain boundary clearance, and the clearance with the T-type membrane was narrower than that with the NaA membrane.

3.2 Adsorption measurement

The water adsorption to zeolite powder is shown in Fig. 3 as a function of feed water concentration. The amount of water adsorbed to NaA powder was very more abounding than that of the T-type powder. Both NaA membrane and T-type membrane were highly water selective adsorption for these mixtures in the same
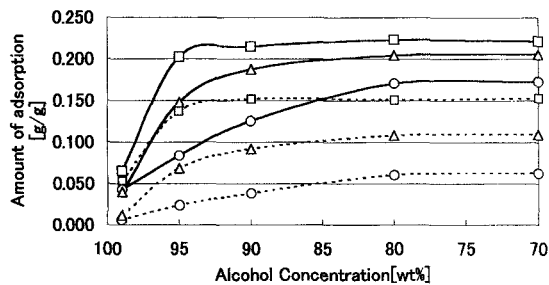
Fig.3 The water adsorption to zeolite powder

—○— NaA-20℃-MeOH   —△— NaA-20℃-EtOH   —□— NaA-20℃-IPA
· O · T-type-20℃-MeOH   · △ · T-type-20℃-EtOH   · □ · T-type-20℃-IPA

manner as the powders. The difference of the amount between the NaA membrane and the T-type membrane was smaller in comparison with the case of zeolite powder. These results suggest that the T-type membrane may be orientated a little and be thicker than the NaA membrane. Moreover, a correlation exists between the solvent polarity and the water adsorbed to the powder, or the membrane. These results indicate that higher the solvent polarity, smaller is the water adsorption to the powder, or the membrane.

3.3 Pervaporation properties

PV experiments were performed with water/alcohol mixtures at various temperatures and a wide range of concentration to study the separation behavior of the NaA membrane and the T-type membrane. Table 1 shows PV properties of both membranes for water/alcohol mixtures. Both of the NaA membrane and the T-type membrane were highly water-permeable for

Table1. PV performance of NaA membrane and T-type membrane for water/alcohol mixtures

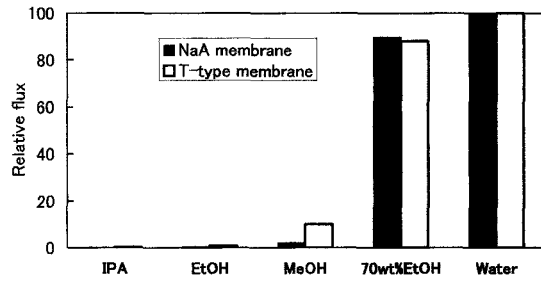| Membrane System		Feed Alcohol [wt%]	Temp. [℃]	Separation Factor α [-]	Flux Q [kgm-2h-1]
NaA	MeOH/Water	90	50	1300	0.51
T		90	50	27	0.65
NaA	EtOH/Water	90	75	10000	2.08
T		90	75	2100	1.18
NaA	IPA/Water	90	75	10000	1.76
T		90	75	10000	1.70

Fig.4 Relative fluxes of pure components through NaA membrane and T-type membrane

these mixtures and displayed extremely high permeation fluxes and separation factors [7-12].

A relative comparison of the pure component fluxes of various alcohols through the NaA membrane and the T-type membrane is respectively shown in Fig. 4.

A correlation seems to exist between the solvent polarity and its flux through the membrane in the same manner as the adsorption results. It appears that higher the solvent polarity, greater is its flux through the membrane in spite of zeolitic type. Though the grain boundary clearance with the T-type membrane is narrower than that with the NaA membrane, it is very interesting to observe that alcohol flux of the T-type membrane is higher than one of the NaA membrane.

An attempt was made to correlate the water permeation flux Q_i for water/alcohol mixtures with partial vapor pressure p_i, calculated by Antoine's equation and Wilson's equation, using Eq. 2.

$$Q_i = K_i(dp_i/dl) = K'_i(p_i - p_o) \qquad (2)$$

Where K'_i is the water permeability coefficient contained membrane thickness l, p_i is the partial vapor pressure of feed side, and p_o is that of permeate side ($p_o \ll p_i$).

Figure 5 shows the dependence of the water flux Q_i through the zeolite membranes on the partial vapor pressure p_i for water/alcohol mixtures. It can be seen that the trend is linear in nature, implying that the water permeability K'_i of the NaA membrane for water/alcohol mixtures is constant. The constancy of the water
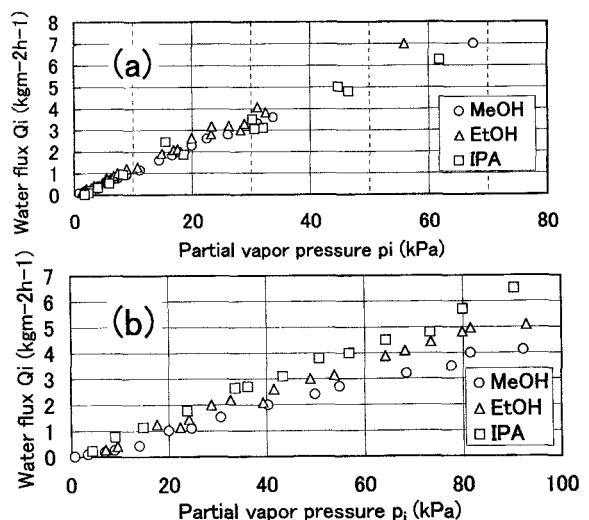
Fig.5 Variation of water flux through Zeolite membranes with feed partial vapor pressure for water/alcohol mixtures
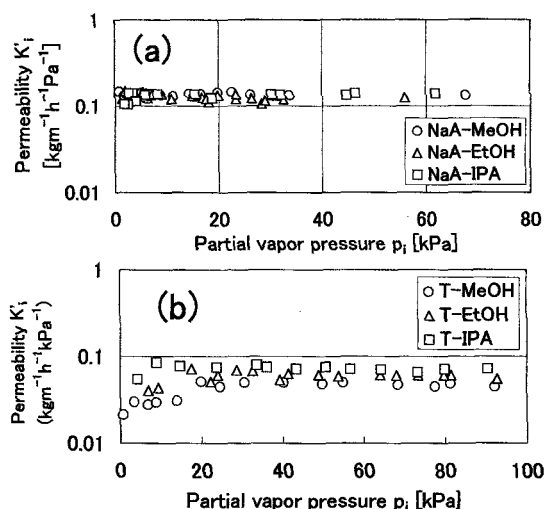(a) NaA membrane (b) T-type membrane

Fig.6 Permeability of zeolite membranes with partial vapor pressure for water/alcohol mixtures.
(a) NaA membrane (b) T-type membrane

permeability K'_i of the NaA membrane shows that there is insignificant interaction between the alcohol molecules and the adsorbed water in the membrane, and also that the coupling effects between the water and alcohol molecules are negligible. On the contrary, the water permeability K'_i of the T-type membrane seems to be dependent on the type of the alcohol, since alcohol competes actively with water of an adsorption site. Especially it may be possible that MeOH, due to its highly polar nature, competes with water in absorbing on the T-type membrane, while the NaA membrane with strong electrostatic sites adsorbs almost only water.

The absorbed amount of zeolite membrane is the sum of amount adsorbed to the crystals on the membrane and one to the grain boundary clearance. The adsorption experimental results indicate that absorbed amount of the crystals on the membrane is very more abounding than one of the grain boundary clearance. In the meantime, the PV experimental results indicate that the grain boundary clearance is an important factor. For that reason, the adsorption equilibrium to the grain boundary clearance should be examined. It is well known that the transport phenomena of porous material with the nano-size pore are taken place by the surface diffusion. Surface diffusion flux Q_i is a product of gradient of an adsorption isotherm dq_i/dl and the surface diffusion coefficient D_{si}, as the following Eq. (3).

$$Q_i = -\rho D_{si}(dq_i/dl) = -\rho D_{si}(dq_i/dp_i)(dp_i/dl) \quad (3)$$
$$-CD_{si}(dq_i/dp_i) = Q_i/(dp_i/dl) = K'_i \quad (4)$$

Where ρ is density of zeolite membrane, C is property of membrane material and constant.

The K'_i of the NaA membrane and the T-type membrane is respectively shown in Fig.6 (a) and (b). Trend of dq_i/dp_i for the NaA membrane seems to be constant, while one for T-type membrane is dependent on the type of the alcohol in the same manner as the powder. In other words, it seems that the absorbed amount of the NaA membrane follows a Henry type adsorption isotherm and its D_{si} is constant. By contrast to the case of the NaA membrane, the sloop for the

adsorbed amount of the T-type membrane is steep when p_i is low. These results indicate that transport phenomena of the T-type membrane are different from ones of the NaA membrane. In view of the present result, transport phenomena of the NaA membrane are mainly caused by the adsorption to the grain boundary clearance, while transport phenomena of the T-type membrane are caused by the adsorption to both of grain boundary clearance and zeolite pore.

4. CONCLUSION

(1) Average Kelvin diameters, which were defined as the diameters at a dimensionless flux of 50%, were 1.4nm for the NaA membrane and 0.8 nm for the T-type membrane, respectively.

(2) Both of the NaA membrane and T-type membrane were highly water selective adsorption for water/alcohol mixtures.

(3) Though the grain boundary clearance with the T-type membrane is narrower than that with the NaA membrane, it is observed that alcohol flux of the T-type membrane is higher than one of the NaA membrane.

(4) The water permeability K'_i of the NaA membrane for water/alcohol mixtures is constant, about 0.13. The water permeability K'_i of the T-type membrane is constant at every alcohol (ca. 0.05 for MeOH, ca. 0.06 for EtOH, ca. 0.075 for IPA), when partial vapor pressure of feed side is over 30 kPa

(5) In view of the present result, transport phenomena of the NaA membrane are mainly caused by the adsorption to the grain boundary clearance, while transport phenomena of the T-type membrane are caused by the adsorption to both of grain boundary clearance and zeolite pore.

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