Transport Properties of Condensable Gases through Microporous Silica Membranes

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The transport properties of condensable gases were studied using sol-gel derived microporous silica membranes. Gas permeation rates of several gas species were measured under many temperature and pressure conditions. The affinities of organic molecules with the silica material were examined through adsorption experiments and analysis of gas state permeation data using a gas permeation model in a micropore potential field. The observed pressure dependency for pure C_2H_6 permeance at a temperature below its critical temperature, T_C showed an almost flat curve in low gas phase pressure region and an abrupt decrease at a specific pressure, the value of which could be comparatively well predicted by the adsorption potential theorem. The permeation experiments for binary mixtures of condensable (C_2H_6, C_3H_8) and non-condensable (N_2) gases were also conducted. In this case, the permeances of the non-condensable gas were smaller compared with those observed in single gas permeation measurements. This fact indicates a condensable component in a micropore would obstruct a non-condensable gas to permeate through the pore. Above mentioned results suggest that the micropore filling of condensable gases could occur in a micropore at temperatures below T_C and at sufficiently high pressures, and this phenomenon would play a significant role in determining the transport properties of these gases through a micropore.
Key words: gas permeation, silica membrane, micropore, condensable gas

1. INTRODUCTION

In recent decades, the development of porous inorganic membranes which have pores of the same order as the molecular size has been reported [1]. It is predicted that they could be applicable to precise and efficient gas separation processes. For example, applications to the separation of hydrogen from organic gas mixtures and carbon dioxide separation from exhaust gas would be promising [2, 3]. Knowledge of the transport mechanisms of gas or vapor within micropores is necessary in order to design a membrane separation unit and to determine the operation conditions for such separation processes.

The gas permeation mechanisms for microporous inorganic membranes with pores less than 1.0 nm in diameter have been extensively investigated in experimental and theoretical manners by many research groups [4-6]. However, those of condensable vapors or organic gases around room temperatures are not clearly understood except for the continuous fluid transport model for nano-scale pores considering the capillary condensation phenomenon [7,8]. In this study, the permeation properties of condensable gases through microporous silica membranes around the critical temperature, T_C of permeants were investigated experimentally.

2. THEORY

Gas state permeation properties through a micropore at temperatures above T_C could be well explained by the gas permeation model, given by Eq. (1), considering the potential field in a micropore, E_P, where P_P is a permeance and k_0 a geometrical factor depending on the pore structure [3].

$$P_p = \frac{k_0}{\sqrt{MRT}} \exp\left(-\frac{E_P}{RT} \right) \qquad (1)$$

On the contrary, at temperatures below T_C, even if the bulk pressure is lower than a saturation pressure of the permeating vapor, a potential field in a micropore would effectively work to compress the permeant and a liquid-like high density phase, which could be called as a 'micropore filling phase', would be formed in a pore. Since a permeating molecule has to move in a micriopore filling phase against the attractive intermolecular interaction, the formation of such a high density phase would lead to decrease the permeance. According to the Polanyi's adsorption potential theorem, the relation between the equilibrium filling pressure, p_f and the external potential energy, which is conpensated with the potential field in a micropore, E_P, is given by Eq. (2) [9],

$$E_p = RT \ln\left(\frac{p_f}{p_{sat}} \right) \qquad (2)$$

where p_{sat} is the saturation pressure at a temperature, T. At bulk pressures above p_f, a micropore filling permeation would occur.

3. EXPERIMENTAL

Gas permeation measurements were performed on microporous silica membranes prepared by the sol-gel

method [3]. The temperature dependencies of permeance for several types of organic and inorganic gases were measured in a temperature range from 300 down to 35 °C under 0.1 MPa in upstream side and evacuated condition in downstream portion. The mean effective pore size for gas pemeartion was roughly evaluated from the molecular size dependency of permeance at 150 °C.

The values of E_P for some organic gases such as C_2H_6, C_3H_8 and C_3H_6 were estimated from their temperature dependencies data of permeance, which were measured at pressures below atmospheric pressure in both the upstream and downstream side, fitted with Eq. (1). The affinity of permeating organic gases with the membrane material was qualitatively studied by gas adsorption experiments for silica powder.

In order to examine the validity of a micropore filling pressure, p_f derived using E_P and to study the permeation property of condensable gases, the pressure dependencies of permeance for C_2H_6 and C_3H_8 were measured in the mean pressure range across a membrane from 5 to 1,500 torr, maintaining the pressure drop constant, at temperatures above and below T_C of those gases.

The permeation experiments of binary mixtures of a condensable organic gas and nitrogen gas as a non-condensable component were also conducted in the condensable gas ratio from zero to 1.0 at a constant total pressure for both sides of a membrane; $p_u = 0.2$ MPa and $p_d = 0.1$ MPa, where p_u is upstream total pressure and p_d downstream one.

4. RESULTS AND DISCUSSION

4.1 Mean effective pore size for gas permeation

Fig. 1 shows the observed permeances of gases for Mem. A and Mem. B as a function of kinetic diameter of permeating molecules. Judging from the deviation from the broken curve predicted by the Knudsen transport model using the molar weight of permeants, both Mem. A and Mem B appear to have effective pores of 4 from 5 Å, and Mem. B has slightly larger size of pores.
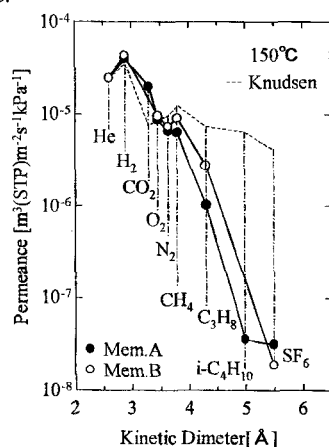

Fig. 1 Permeance vs. kinetic diameter for several gas species.

4.2 Temperature dependencies of permeance

Figs. 2 and 3 show the Arrhenius plots of the observed permeance of several inorganic and organic

gases for Mem. A. As shown in Fig. 2, the temperature dependencies of permeance for inorganic gases, whose critical temperatures were much lower than room temperature, were well fitted with Eq. (1) for all operation temperatures.
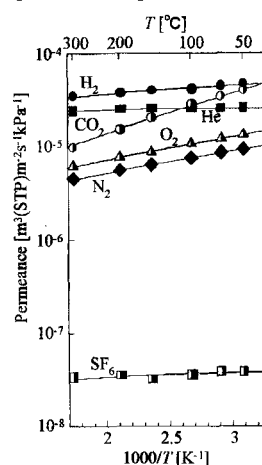

Fig. 2 Dependencies of permeance on temperature for Mem. A (curves fitted with Eq. (1); $p_u = 0.1$ MPa, p_d = evacuated)
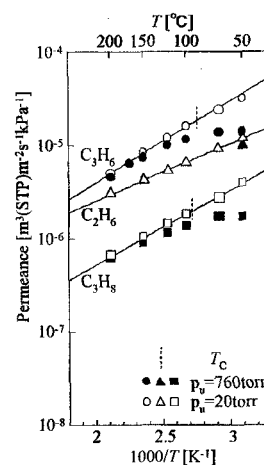

Fig. 3 Dependencies of organic gas permeance on temperature for Mem. A (curves fitted with Eq. (1); p_d = evacuated)

Table I E_P in Eq. (1) obtained from fitting to temperature dependencies of permeance and predicted filling pressure, p_f in Eq. (2)

		E_P [kJ/mol]	T [°C]	p_{sat} [torr]	p_f [torr]
Mem.A	C_2H_6	-10.0	25	31,700	559.9
	C_3H_8	-13.6	50	12,900	80.6
			70	19,400	163.4
	C_3H_6	-15.1	70	22,800	114.6
Mem.B	C_3H_8	-12.7	50	12,900	113.8
			70	19,400	226.3
	C_3H_6	-13.6	70	22,800	193.9

On the contrary, in Fig. 3, the permeances of C_3H_8 ($T_C = 96.8$ °C) and C_3H_6 ($T_C = 91.8$ °C) at temperatures around and below T_C were smaller than the values expected from the dependency curves in high temperature region. Since Eq. (1) could be well fitted to permeances observed in an operation condition of lower upstream pressure, $p_u = 20$ torr, for all temperatures, it is suggested that the formation of a micropore filling phase would lead to decrease in permeance of condensable gases. The values of E_P for C_2H_6, C_3H_8 and C_3H_6 were estimated using the temperature dependency curves in the case of $p_u = 20$ torr to be fitted with Eq. (1). The permeances of C_3H_8 and C_3H_6 on Mem. B were also measured and the values of E_P were calculated in the same manner. The obtained values of E_P for Mem. A and Mem. B and the predicted values of micropore filling pressure, p_f by using Eq. (2) are summarized in Table I.

4.3 Adsorption isotherm

Fig. 4 shows the observed adsorption isotherms for C_2H_6, C_3H_8 and C_3H_6 on silica powder at 35 °C. The silica powder was prepared by drying silica colloidal sol solution, which was used in silica membrane preparation,

and fired for 3 hours at 500 °C. The specific surface area (BET surface area) of the powder estimated from an N_2 adsorption measurement at 77 K was 717 [m^2/g-powder]. The amount of adsorbed C_3H_8 was larger than that of C_2H_6 and that of C_3H_6 was the largest of three measured gas species at any identical equilibrium gas phase pressure. These results are qualitatively in good agreement with the estimated values of E_P listed in Table I. The affinity of C_3H_8 with the silica surface must be relatively large compared with that of C_2H_6 judging from the adsorption isotherms, and this is clearly shown in the larger absolute value of E_P obtained from gas permeation experiments. This is true for C_3H_6. These findings would support the validity of the value of E_P and resultant p_f.
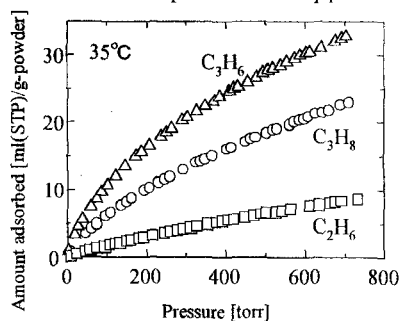

Fig. 4   Adsorption isotherms of organic gases for silica powder at 35 °C

4.4 Pressure dependencies of permeance

Figs. 5 and 6 show the observed permeances of pure C_2H_6 and C_3H_8, respectively, plotted against the mean pressure of the upstream and downstream region for Mem. A at several temperatures above and below T_C. The pressure differences across a membrane, Δp were controlled to be nearly identical around 50 torr for all data points. At temperatures above T_C, both the permeances of C_2H_6 and C_3H_8 were nearly constant independent of operation pressure. Gas state permeation might occur at these temperatures. On the contrary, at temperatures below T_C, both the permeances of C_2H_6 and C_3H_8 decreased with increasing pressure. In Fig. 5, the permeance largely decreased around the mean pressure of predicted p_f. Therefore, it is suggested that a decrease in permeance of a condensable gas would be caused by formation of a micropore filling phase in a pore. The mobility of permeating molecules in such a dense phase might be probably smaller compared with that in gas phase. The observed slight decrease in C_2H_6 permeance at pressures below p_f might be due to the existence of pore size distribution. Concerning the C_3H_8 permeance, at temperatures below T_C, it largely and continuously decreased with increasing mean pressure even at pressures below p_f. In this case, an effect of pore size distribution should be taken into consideration as well. Another possible explanation is that, when the molecular size of C_3H_8 was close to the pore size, the mobility of C_3H_8 molecules could be smaller even without formation of a filling phase. In such a small pore, permeating molecules must be forced to be closely surrounded by pore walls which have larger interaction with permeating molecules than intermolecular interaction.
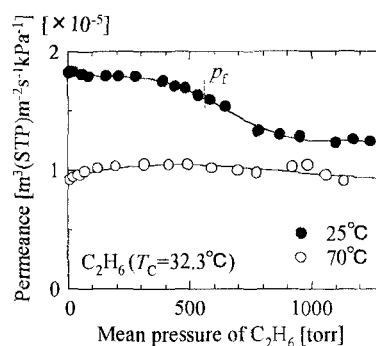

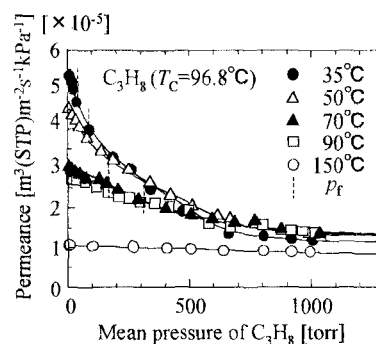Fig. 5   Dependencies of C_2H_6 permeance on the mean pressure for Mem. A.

Fig. 6   Dependencies of C_3H_8 permeance on the mean pressure for Mem. A.

4.5 Permeation of binary gas mixtures

In order to examine the effect of co-existent condensable gas on non-condensable gas permeation, the permeation experiments of binary mixtures of an organic gas and N_2 were conducted. Figs. 7 and 8 show the observed dependencies of permeance of each component on the mean partial pressure of C_2H_6 in permeation of N_2/ C_2H_6 gas mixture for Mem. A. The upstream total pressure was 0.2 MPa and downstream 0.1 MPa. At a temperature above T_C of C_2H_6, 70 °C, both the permeances of N_2 and C_2H_6 were independent of the partial C_2H_6 pressure or C_2H_6 ratio in upstream and downstream gas phase. This means that both the gases permeated through the membrane in gas state without being obstructed by the other component. On the contrary, at a temperature below T_C of C_2H_6, 25 °C, the permeance of C_2H_6 most largely decreased around p_f as could be seen in single gas permeation of C_2H_6. The observed N_2 permeance also decreased with increasing partial C_2H_6 pressure. These results suggest that co-existent C_2H_6 would be obstructive to the permeation of non-condensable N_2 at a temperature below T_C.

Fig. 9 show the partial pressure dependencies of N_2 and C_3H_8 permeances for N_2/C_3H_8 gas mixture at a temperature below T_C of C_3H_8, 50 °C on Mem. B. Judging from the results of adsorption experiments and the values of E_P, C_3H_8 has larger interaction with pore surface than C_2H_6. In addition, the condensability of C_3H_8 is also larger than that of C_2H_6. Therefore, it is expected that a firmer micropore filling phase of C_3H_8 could be formed in a pore. Concerning the permeation of C_3H_8, the permeance decreased with increasing partial C_3H_8 pressure and the pressure dependency was nearly same as that observed in permeation of pure C_3H_8. The

N_2 permeance also decreased with increasing C_3H_8 component. The observed decreasing rate of N_2 permeance along with increase in C_3H_8 ratio in gas phase for permeation of N_2/C_3H_8 gas mixture was greater than that in Fig. 8 for N_2/C_2H_6 system. Therefore C_3H_8 molecules might be more firmly adsorbed or filled in a micropore and they could more strongly obstruct N_2 molecules to permeate through the pore than C_2H_6.
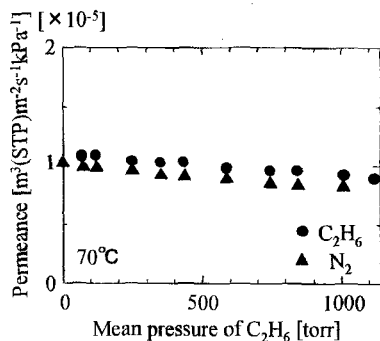

Fig. 7   Dependencies of N_2 and C_2H_6 permeance on the mean pressure of C_2H_6 in permeation of N_2/C_2H_6 gas mixtures for Mem. A at a temperature above T_C of C_2H_6, 70 °C.
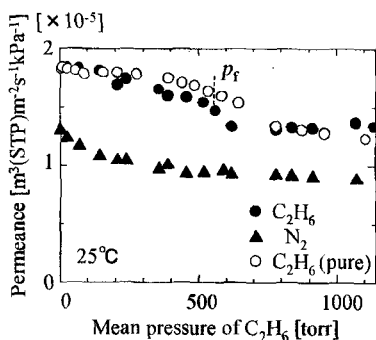

Fig. 8   Dependencies of N_2 and C_2H_6 permeance on the mean pressure of C_2H_6 in permeation of N_2/C_2H_6 gas mixtures and pure C_2H_6 for Mem. A at a temperature below T_C of C_2H_6, 25 °C.
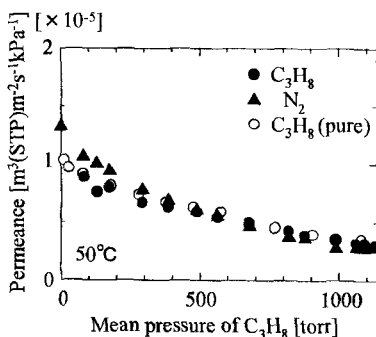

Fig. 9   Dependencies of N_2 and C_3H_8 permeance on the mean pressure of C_3H_8 in permeation of N_2/C_3H_8 gas mixtures and pure C_3H_8 for Mem. B at a temperature below T_C of C_3H_8, 50 °C.

5. CONCLUSIONS

The transport properties of condensable gases in a micropore were examined by gas permeation experiments of pure gases and N_2/organic gas mixtures using sol-gel derived microporous silica membranes whose pore sizes were several angstroms. Observed permeation properties of inorganic gases were well explained by a gas permeation model considering the potential field in a micropore, while concerning the transport properties of condensable organic gases, a critical temperature of which is relatively high, the permeance tends to decrease with decreasing temperature or increasing pressure of gas phase. The observed pressure dependencies of pure C_2H_6 permeance at 25 °C showed an almost flat curve in low gas phase pressure region and largely decreased around a micropore filling pressure, p_f which could be well predicted by the adsorption potential theorem using the value of potential in a micopore, E_p estimated from the temperature dependency curve of permeance. The pure C_3H_8 permeance at temperatures below T_C largely and continuously decreased with increasing mean pressure even at pressures below p_f. In this case, the molecular size of a permeating molecule which was very close to the pore size might affect the mobility of adsorbed molecules at relatively low pressure region. The pressure dependencies of C_2H_6 and C_3H_8 permeances observed in permeation experiments for binary gas mixtures of N_2/C_2H_6 and N_2/C_3H_8 were nearly same as those in the single organic gas permeations, while N_2 permeances decreased with increasing partial organic gas pressures at temperatures below T_C of co-existent organic gases, especially in permeation of N_2/C_3H_8 gas mixture. These findings suggest that those molecules of condensable gases strongly adsorbed or filled in a micropore would decrease the mobility of own themselves and also could obstruct co-existent N_2 to permeate through the pore to decrease its permeance as well.

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