

Nomenclature

$B(v, P)$	= function defined by Eq. (6-4)	[—]
$FA(v, P)$	= function defined by Eq. (8-1)	[—]
$FB(v, P)$	= function defined by Eq. (8-2)	[—]
$FFA(v, P)$	= function defined by Eq. (6-2)	[—]
$FFT(v, P)$	= function defined by Eq. (6-3)	[—]
Kn	= Knudsen number	[—]
K_0	= Knudsen permeability	[m ³ (STP) · m · s ⁻¹ · m ⁻² · Pa ⁻¹]
L	= dimensionless distance from membrane surface ($L=l/l_m$)	[—]
l	= distance from membrane surface	[m]
l_m	= thickness of membrane	[m]
P	= dimensionless pressure ($P=p/p_h$)	[—]
p	= local pressure along permeation	[Pa]
Q	= dimensionless flow rate of high-pressure stream ($Q=q/q_f$)	[—]
Q'	= dimensionless flow rate of low-pressure stream ($Q'=q'/q_f$)	[—]
q_f, q, q'	= volume flow rates on feed point, high-pressure stream and low-pressure stream, respectively	[m ³ (STP) · s ⁻¹]
S	= membrane area	[m ²]
S_d	= dimensionless membrane area defined by Eq. (6-1)	[—]

T	= temperature	[K]
v, x, y	= mole fractions of component A at an arbitrary $L, L=0$ and $L=1$, respectively	[—]
α	= stage separation factor defined by $y_p(1-x_o)/\{x_o(1-y_p)\}$	[—]
α_0	= ideal separation factor defined by the ratio of $K_{0,A}/K_{0,B}$	[—]
θ	= stage cut defined by ratio of permeate flow to feed flow (Q_p/Q_f)	[—]

<Subscripts>

A	= lighter component
B	= heavier component
f	= feed point
h	= high-pressure side
i	= initial point of integration ($Q'=0$)
l	= low-pressure side
o	= outlet point
p	= permeate

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PERMEATION OF GASES THROUGH A SYMMETRIC CELLULOSE ACETATE MEMBRANE

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Key Words: Membrane Permeation, Gas Permeability, Gas Diffusivity, Symmetric Cellulose Acetate, Time Lag Method

Cellulose acetate (CA) is a very popular polymer and asymmetric membranes are commercially used for separations of mixed gases. Data of permeability through the CA symmetric dense membrane are required to understand the mechanism of gas permeation through asymmetric membranes. However, gas permeation properties of the dense membrane have not been measured sufficiently.^{2,3,5,6,9} Therefore, the objective of this work is to measure the permeation properties of the CA dense membrane to

hydrogen, helium, methane, nitrogen, carbon monoxide, oxygen, carbon dioxide, argon and propane in the temperature range of 273 to 373 K by using the conventional "time-lag" method.

1. Experimental

A CA dense membrane of 20 μ m thickness was prepared by casting a 25 wt% CA (Eastman Chemical Co., Ltd., E398-3) acetone solution on a flat glass plate at room temperature and evaporating acetone for one week.

Membrane samples were further dried in the time-

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lag apparatus at the maximum measuring temperature (373 K) for one day before the permeability measurement.

The gases used were supplied by the Nihon Sanso Co. (H_2 , He, CH_4 , N_2 , CO, O_2 , Ar and CO_2) and the Takachiho Kagaku Co. (C_3H_8) and were 99.9% pure at least.

The permeabilities and time lags were measured, using the high vacuum time-lag technique of Barrer.¹⁾ The apparatus employed in this study was similar to that described by Huvard *et al.*⁴⁾ and the experimental procedure was conventional. The permeability was determined by a slope of time-pressure curve and the diffusivity, D_θ , was calculated from the following equation.

$$D_\theta = \frac{l^2}{6\theta} \quad (1)$$

When the observed time lag was less than 20 sec, D_θ was not calculated in this work to avoid uncertainty.

It is said that CA is in the glassy or partially glassy state in the temperature range of this experiment.¹⁰⁾ The transport behavior of glassy polymer membranes is known to follow the dual sorption and dual mobility model,^{7,8)} so that the permeabilities and diffusivities measured by the time-lag method are apparent properties.

2. Results and Discussion

The permeability and diffusion coefficients of various gases in CA membrane are shown in the form of Arrhenius plots in Figs. 1 and 2. Most of the measurements were made in the temperature range 273 to 373 K. The linearity of the Arrhenius plots is almost satisfactory. The apparent activation energies for permeation and for diffusion are summarized in Table 1.

The apparent activation energies for permeation are smaller than those for diffusion; this arises from the fact that the apparent heats of solution of all gases are negative ($-23 \sim -17$ KJ/mol).

Figures 1 and 2 show literature values also: permeability coefficients of He and Ar measured by Gantzel *et al.*,³⁾ and permeability and diffusion coefficients of O_2 and CO_2 measured by Stern *et al.*⁹⁾ Our data are in good agreement with the data of Gantzel *et al.* but deviate slightly from those of Stern *et al.* Furthermore, the apparent activation energies of Stern *et al.* are somewhat larger than our values and breakpoints clearly exist around 333–343 K in permeabilities and diffusivities for several gases.

A deviation of 20–30% between data measured by different investigators is often observed. However, it is important to distinguish whether the deviation is due to experimental error or to the difference of polymer structure. Gantzel *et al.* prepared the CA

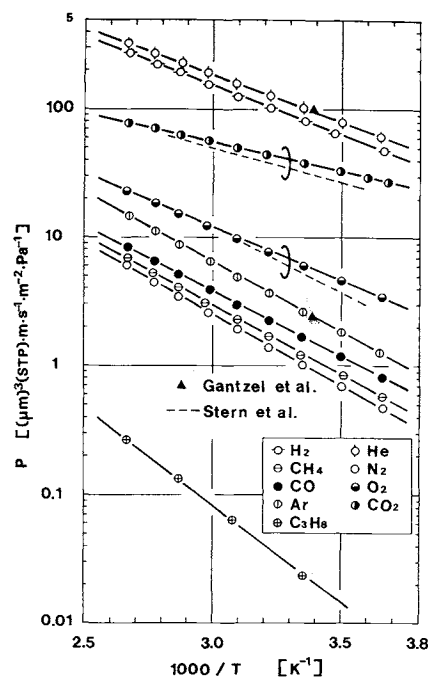


Fig. 1. Temperature dependence of permeability of cellulose acetate dense membrane to various gases.

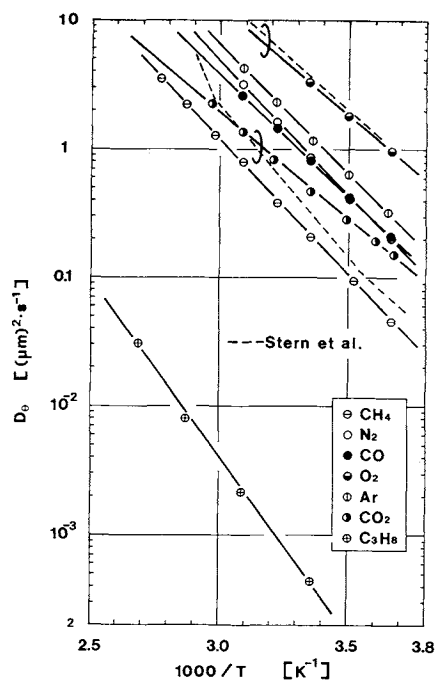


Fig. 2. Temperature dependence of diffusivity of cellulose acetate dense membrane to various gases.

dense membrane by casting an acetone solution of 39.4% acetyl content CA, which was almost equal to that used in this work. Stern *et al.*^{9,10)} prepared it by directly drying an asymmetric CA membrane for reverse osmosis whose acetyl content was the same as that of our membrane.

The difference of transport properties between this work and that of Stern *et al.* work may be caused by differences in polymer structure which depend on the

Table 1. Apparent activation energies for permeation and diffusion of some gases through cellulose acetate dense membrane

Gases	E_p [KJ/mol]	E_d [KJ/mol]
H ₂	14.8	
He	14.4	
CH ₄	20.7	40.9
N ₂	21.5	40.6
CO	19.7	36.9
O ₂	16.2	34.0
Ar	20.8	38.1
CO ₂	8.95	32.4
C ₃ H ₈	30.0	51.9

membrane preparation process.

Acknowledgement

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Nomenclature

D_θ = apparent diffusion coefficient calculated from Eq. (1) [m²·s⁻¹]

E_p = apparent activation energy for permeation [KJ·mol⁻¹]
 E_d = apparent activation energy for diffusion [KJ·mol⁻¹]
 l = membrane thickness [m]
 P = apparent permeability coefficient [m³(STP)·m·s⁻¹·m⁻²·Pa⁻¹]
 θ = time lag [s]

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DYNAMIC DRYING OF BENZENE WITH ION-EXCHANGE RESIN

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Key Words: Adsorption, Desorption, Drying, Isotherm, Ion Exchange Resin, Moisture, Benzene

Various organic solutions are used in many industries such as the petrochemical industry. The presence of moisture in those solvents results in poor insulation, corrosion of apparatus and catalyst poisoning. Therefore, the moisture content of the solvents must be reduced to less than several ppm.

Since ion exchange resins have an ability to adsorb selectively polar substances from nonpolar solvents, they have been used for the drying of organic solvents.⁴⁾ In the previous paper,²⁾ a cation-exchange resin was shown to be excellent in the drying of

nonpolar solvent such as benzene, and its capacity to adsorb water varied greatly with temperature.

In this study, periodic adsorption and desorption were investigated to utilize the great temperature dependency and the reversibility of adsorption equilibria of the resin-water system. A tapered column was used to reduce the pressure drop due to expansion of the resin.

1. Principle of Adsorption and Desorption Process

Adsorption isotherms are always linear and there are significant differences of adsorption capacity between 283 K and 333 K. The solubilities of water in benzene are 0.396 and 1.44 kg/m³ at 283 K and 333 K.

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