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Temperature and Pressure Dependence of Gas Permeability through Inhomogeneous Polymer Membranes

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Transport parameters of gas through a polymer membrane, in which a small amount of porous regions are included, are discussed as functions of pressure and temperature. It is evidenced that pore flow can be divided from the flow through the polymer matrix if the polymer structure is stabilized against applied pressure and/or temperature changes.

KEYWORDS : Membrane / Pore flow / Solution diffusion

1. INTRODUCTION

Recently synthetic polymers have been used as gas separation membranes for hydrogen recovery from oil gas, carbon dioxide separation from earth gas and oxygen enrichment from air. These membranes consist of asymmetric or composite structure. The active layer which plays the main role in gas separation has a dense structure. Pore existence in the dense layer reduces the gas separation efficiency. It is important to characterize the pores in a dense polymer membrane. Measurement of pressure or temperature dependence on the gas permeability coefficient is an effective method of evaluating the existence of pores in polymer membranes.

According to the membrane transport mechanism, synthetic polymer membranes are classified in two categories, i.e., dense and porous membranes, respectively. In dense membranes, "vacant space" in the polymer changes in size and position over time[1]. Therefore diffusion of small molecules is influenced by micro-Brownian motion of the polymer chains. On the other hand, "vacant space" in porous membranes is fixed in size and position over time. In this case, the mobility of penetrant molecules is not affected by the polymer molecule, and the permeability coefficient is much higher than that of the dense membrane.

Gas transport through a dense polymer membrane is explained by the solution and diffusion mechanism, where gas is solubilized into the polymer surface as a liquid, diffuses across the polymer and then evaporates from the opposite surface. Solubility obeys Flory-Huggins' theory and the diffusion coefficient free volume theory above the glass transition temperature. On the other hand both theories cannot be exactly applied below glass tran-

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sition temperature at this moment because of the thermodynamically nonequilibrium states of the polymer. The pressure dependence of the transport parameter in a dense polymer is explained as follows. For a rubbery polymer, the permeability coefficient is nearly constant and increases with pressure at comparatively high pressure because of the pressure dependence of solubility and diffusion coefficients. For a glassy polymer, the permeability coefficient decreases with pressure increase on the low-pressure side as a consequence of the interaction between polymer and gas molecules, and becomes a constant value before the beginning of polymer plasticization by the penetrant at comparatively high pressure. The temperature dependence of the transport parameter is explained as follows. Diffusion coefficients above and below the glass transition temperature are proportional to the reciprocal temperature, that is, they follow the Arrhenius relationship(1,2).

In the case of the porous polymer membrane, gas flow is represented by Darcy's law. If the mean free path of gas molecules is much smaller than the pore diameter, gas flow is described as viscous flow. If the mean free path is much larger than the pore diameter, it is illustrated as Knudsen flow. The permeability coefficient of the former is proportional to the mean pressure between high- and low-pressure sides. On the other hand, that of the Knudsen flow is constant regardless of pressure. The temperature dependence of the permeability coefficient of viscous or Knudsen flow is different from that of diffusive flow. Since gas density in the pore is inversely proportional to the temperature, the permeability coefficient of viscous flow is proportional to the reciprocal temperature, and taht of Knudsen flow, to the square root of reciprocal temperature(3,4).

If the gas transport mechanism is ruled by viscous or knudsen flow the membrane is considered to be a porous medium. In this case it is not very difficult to calculate the membrane structural parameters such as mean pore size, porosity and tortuosity, since the effects from the polymer matrix can be ignored. If the number of pores is insufficient in the membrane, it is difficult to evaluate those structural parameters according to the porous media, since the penetrant flows from both polymer matrix and pores must be evaluated. In this paper, separation of two contributions of gas flows is discussed to precisely evaluate the membrane transport parameters in a pinholed dense membrane.

2. THEORY

A membrane possessing small penetrating channels through a polymer matrix is shown in figure 1, where the flow in the perpendicular y and z directions can be neglected(5). C(x, t), $C_p(x, t)$, and p(x, t) are the concentration of dissolved and diffusing gas in the polymer matrix, the average total gas concentration in all channels, and gas pressure at x, respectively. $C_p(x, t)$ is shown as

$$C_p(x, t) = \varepsilon p(x, t)/RT, \qquad (1)$$

where R is the gas constant, T absolute temperature, and ε a constant proportional to the total channel volume. Gas present in the channels dissolves in the adjoininig polymer matrix at a rate given by $K_s p(x, t)$. Gas dissolved in polymer evaporates at the channel surface with a rate given by $K_e C(x, t)$. For channel diameter larger than the mean free path

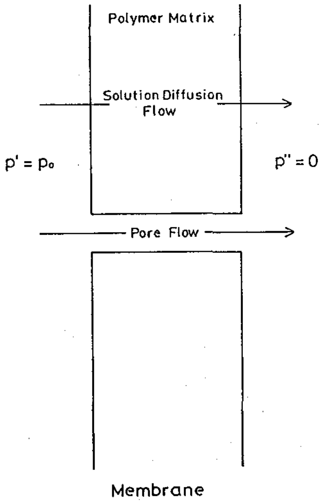

Figure 1. Schematic diagram of inhomogeneous polymer membrane.

of gas, the flow becomes viscous. The convection velocity is

$$v(C_p)=(K'/\eta)(dp/dx)=\gamma(dC_p/dx). \tag{2}$$

Applying the principle of mass convection, the change of C(x, t) with time is due to the three effect: diffusion in the polymer matrix, loss due to evaporation from the polymer matrix to channels and gain due to solution from channels to the polymer matrix.

$$d\,C(x, t)/d\,t=d\{Dd\,C(x, t)/d\,x\}\,/d\,x+K_s p(x, t)-K_e C(x, t) \tag{3}$$

The change of $C_p(x, t)$ with time is also due to three effects: convection of gas in the channels, gain due to the evaporation of dissolved gas from the polymer matrix to channels, and loss due to the solution of gas from channels to the polymer matrix.

$$d\,C_p(x, t)/d\,t=d\{v(C_p)C_p(x, t)\}/d\,x-K_s p(x, t)+K_e C(x, t) \tag{4}$$

The total gas concentration in the membrane $C_t(x, t)$ becomes

$$C_t(x, t)=C(x, t)+C_p(x, t). \tag{5}$$

Change of the total gas concentration with time in the membrane becomes, from eqs. (3), (4) and (5),

$$d\,C_t(x, t)/d\,t=d\{Dd\,C(x, t)/d\,x+v(C_p)C_p(x, t)\}/d\,t. \tag{6}$$

Since solution equilibrium is attained instantaneously at the membrane surface, the boundary conditions are simplified:

$$C_t(0,\ t)=C(0,\ t)+C_p(0,\ t)=S_o p_o+\varepsilon p(0,\ t)/RT \tag{7}$$

$$C_t(1,\ t)=C(1,\ t)+C_p(1,\ t)=S_o p(1,\ t)+\varepsilon p(1,\ t)/RT=0, \tag{8}$$

where S_o is the solubility parameter and $p(1,\ t)=0$.

At the steady-state permeation of the membrane, which has the thickness of 1, the permeability coefficient is found to be

$$P=-q_s l/p_o=D_o S_o+\pi p_o, \tag{9}$$

where q_s is steady state gas flux and

$$\pi=\gamma\varepsilon^2/2(RT)^2. \tag{10}$$

The time lag θ is also calculated from eq. (6) and Frisch's method as[6)]

$$\theta=(1+\beta)l^2/6D_o\{1+(\pi/D_o S_o)p_o\}. \tag{11}$$

If the local solution equilibrium has been attained,

$$K_s p(x,\ t)=K_s C_p(x,\ t)RT/\varepsilon=K_e C(x,\ t). \tag{12}$$

At steady state $C_t(x,\ \infty)$, the ratio of C and C_p is considered to be constant.

$$C_p(x,\ \infty)=\beta C(x,\ \infty) \tag{13}$$

From eqs. (12) and (13),

$$\beta=(K_e/K_s)(\varepsilon/RT)=\varepsilon/S_o RT, \tag{14}$$

where

$$K_s/K_e=S_o \tag{15}$$

and

$$\pi=\gamma\varepsilon^2/2(RT)^2=\gamma\beta^2 S_o^2/2. \tag{16}$$

If the membrane is pore free, time lag becomes

$$\theta(\text{pore free})=\theta_o=l^2/6D_o. \tag{17}$$

Equation (11) is rewritten as

$$\theta=(1+\beta)\theta_o/\{1+(\pi/D_oS_o)p_o\}. \qquad (18)$$

Equation (18) is also rewritten as

$$1/\theta=1/(1+\beta)\theta_o+\pi p_o/(1+\beta)\theta_oD_oS_o. \qquad (19)$$

The diffusion coefficient which is calculated by the time lag method in the pore membrane is found to be

$$D=D_o/(1+\beta)+\pi p_o/(1+\beta)S_o, \qquad (20)$$

where

$$D_o=l^2/6\theta_o \text{ and } D=l^2/6\theta. \qquad (21)$$

The solubility parameter of pore membrane which is calculated by the time lag method is shown as

$$S=P/D=(1+\beta)P_o/D_o=(1+\beta)S_o \qquad (22)$$

The temperature dependence of the permeability coefficient, diffusion coefficient and solubility parameter of the polymer matrix obeys the Arrhenius relationship[1], that is,

$$P_o=P_o^o\exp(-E_P/RT) \qquad (23)$$
$$D_o=D_o^o\exp(-E_D/RT) \qquad (24)$$
$$S_o=S_o^o\exp(-\triangle H/RT), \qquad (25)$$

where

$$E_P=E_D+\triangle H, \qquad (26)$$

and E_P is the activation energy of permeation, E_D apparent activation energy of diffusion and $\triangle H$ enthalpy of solution.

The temperature dependence of the permeability coefficient of convective flow is indicated as[3,4].

$$P_{vi}=A/T \quad \text{for viscous flow} \qquad (27)$$
$$P_{kn}=B/T^{1/2} \quad \text{for Knudsen flow,} \qquad (28)$$

where A and B are constants.

The permeability coefficient, including convective flow and polymer matrix flow, which is shown in eq. (9), can be refined using eqs. (23), (24), (27) and (28) as

$$P=D_oS_o+\pi p_o=P_o+P_{vi}=P_o{}^o\exp(-E_P/RT)+A/T \tag{29}$$

or

$$P=P_o+P_{kn}=P_o{}^o\exp(-E_D/RT)+B/T^{1/2} \tag{30}$$

The diffusion coefficient given by the time lag method, including convective flow and polymer matrix flow, which is shown in eq. (20), can also be found using eqs. (23), (24), (27) and (28) for viscous flow as

$$\begin{aligned} D&=D_o/(1+\beta)+\pi p_o/(1+\beta)S_o \\ &=\{D_o/(1+\beta)\}\{1+\pi p_o/D_oS_o\} \\ &=\{D_o/(1+\beta)\}\{1+P_{vi}/P_o\} \\ &=\{D_o/(1+\beta)\}\{1+A/P_o{}^oT\exp(-E_D/RT)\} \end{aligned} \tag{31}$$

and for Knudsen flow,

$$\begin{aligned} D&=\{D_o/(1+\beta)\}\{1+P_{kn}/P_o\} \\ &=\{D_o/(1+\beta)\}\{1+B/P_o{}^oT^{1/2}\exp(-E_D/RT)\}. \end{aligned} \tag{32}$$

3. EXPERIMENTAL

3.1. Samples

Homogeneous CA and poly(chloro-p-xylylene)(Palyrene C) were prepared. The thicknesses of CA and Palyrene C were 89.0μm and 16.9μm, and 5.9μm, respectively.

3.2. Measurements

The gas permeability measurement was performed by the high-vacuum method. The pressure increases in the low-pressure compartment were recorded as a function of time. The apparent diffusion coefficients were then obtained from time-lag (θ), and the permeabilities, from the slope of the asymptote of the p″-versus-t curve (p″=pressure in the low-pressure compartment). The solubility S of the gas in the membrane was obtained from the relationship P=SD.

4. RESULTS and DISCUSSION

4.1. Pressure Dependence of Transport Parameter

In figure 2, the permeability coefficients of nitrogen gas through a cellulose acetate membrane which has the thickness of 16.9μm are shown as a function of feed pressure p_o at 25°C. The thickness of this membrane is sufficient to allow pinholes across the membrane surface to surface. The permeability coefficient decreases below 3atm and increases above 4atm with pressure increase above 4atm. Equation(9) can be be applied to the permeability coefficients above 5atm, and is shown as the solid line. The slope π and the intercept

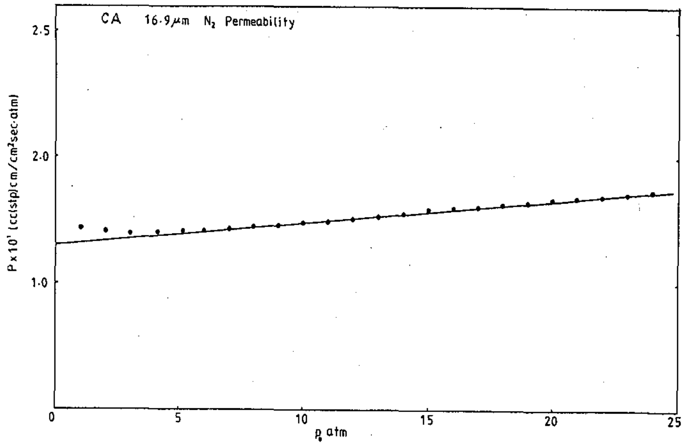

Figure 2. Permeability coefficient of N_2 gas through cellulose acetate membrane whose thickness is 16.9μm, as a function of feed pressure.

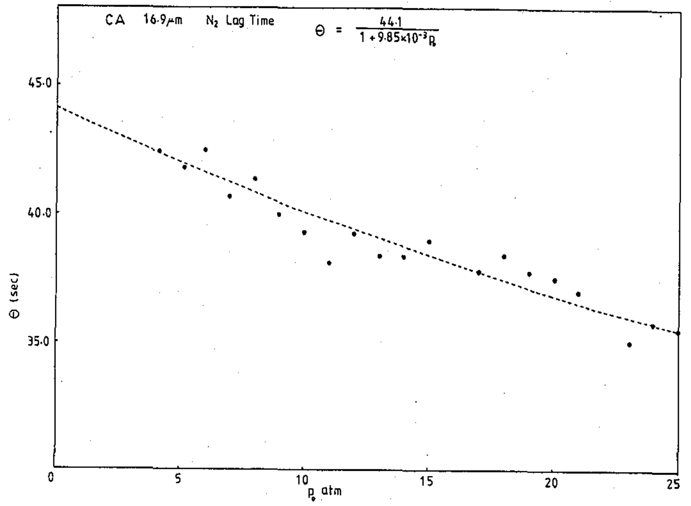

Figure 3. Time lag in N_2 gas permeation through cellulose acetate membrane whose thickness is 16.9μm, as a function of feed pressure.

D_oS_o are calculated as 1.80×10^{-11} (cm^3(stp)·cm/cm^2·atm^2) and 1.30×10^{-9} (cm^3(stp)·cm/cm^2·atm), respectively, and π/D_oS_o is found to be 1.38×10^{-2}.

In figure 3, time lags are plotted as a function of feed pressure. Applying time lag data to eq. (19), $1/(1+\beta)\theta_o$ and $\pi/(1+\beta)\theta_oD_oS_o$ are given from the intercept and slope, respectively. Using these data time lags are calculated again and plotted as the dotted line in figure 3. π/D_oS_o is also calculated to be 9.85×10^{-3}, which corresponds with the result based on permeability coefficients. Since apparent diffusion and solubility coefficients of nitrogen gas in the homogeneous dense cellulose acetate membrane whose thickness is 89μm can be determined by the time lag method using P=DS, porosity ε is estimated using eqs. (14) and (17), and $1/1(1+\beta)\theta_o$. It is shown that the porosity of this membrane is about 0.101%⁷⁾.

4.2. Temperature Dependence of Transport Parameter

Equations (29) and (30) show the temperature dependence of the gas permeability coefficient across a membrane which has both convective and diffusive flow originating from the pores and the polymer matrix at the same time. Permeability coefficients of nitrogen and helium gases, which were calculated from eq. (29) using the data from the cellulose acetate membrane, are shown as a function of reciprocal temperature in figures 4 and 5, respectively. α^* means the ratio of the viscous permeability coefficient to the diffusive one. Increase of α^* indicates that pore flow becomes predominant. The permeability coefficient decreases at high temperature and increases at low temperature with temperature decrease.

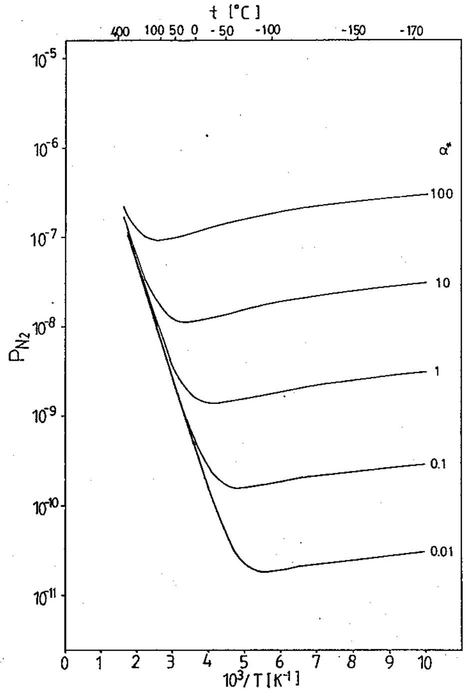

Figure 4. Permeability coefficient of N_2 gas through a polymer membrane which has a small amount of pinholes, as a function of reciprocal absolute temperature with various permeability ratios of pore flow to solution diffusion flow.

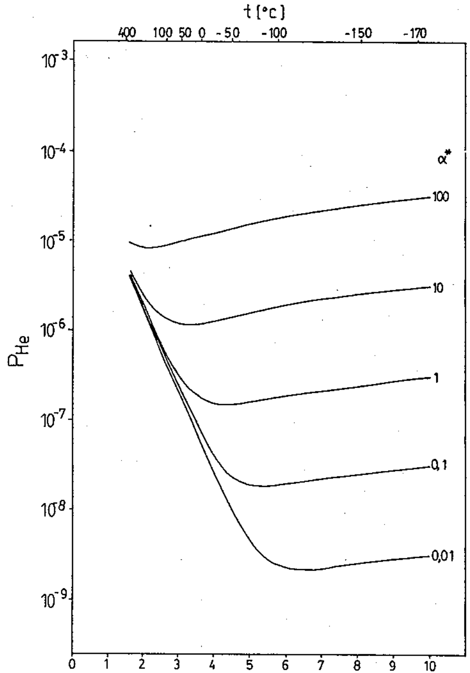

Figure 5. Permeability coefficient of He gas through a polymer membrane which has a small amount of pinholes as a function of reciprocal absolute temperature with various permeability ratios of pore flow to solution diffusion flow.

Equations (31) and (32) show the temperature dependence of apparent gas diffusion coefficients across the same membrane. Apparent diffusion coefficients of nitrogen and helium gases, which were calculated from eq. (31) also using the data from the cellulose acetate membrane, are shown as a function of reciprocal temperature with various α^* in figures 6 and 7, respectively. The apparent diffusion coefficient of nitrogen gas decreases with temperature decrease and discontinuities are observed. On the other hand, apparent diffusion coefficients of helium gas are indicated by the different figures. At high temperature diffusion coefficients decrease with temperature decrease, and at low temperature they increase with temperature decrease. Such an abnormality in the apparent diffusion coefficient is caused by the positive value of the enthalpy of solution. Even if the flow mechanism in pores is Knudsen flow, similar phenomena are observed[7].

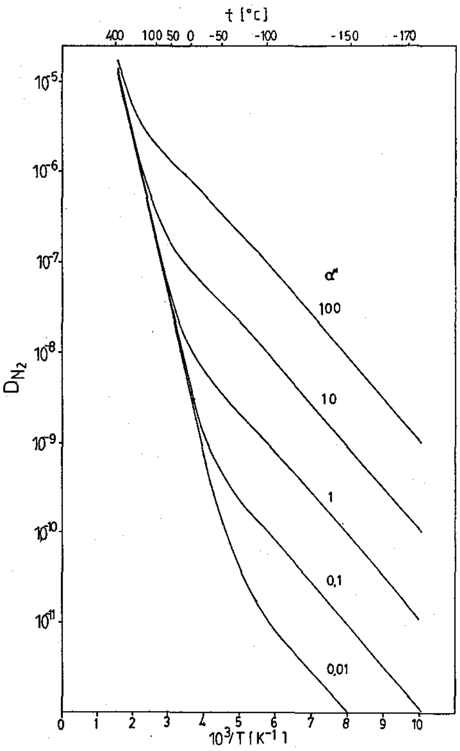

Figure 6. Apparent diffusion coefficient of N_2 gas through a polymer membrane which has a small amount of pinholes, as a function of reciprocal absolute temperature with various permeability ratios of pore flow to solution diffusion flow.

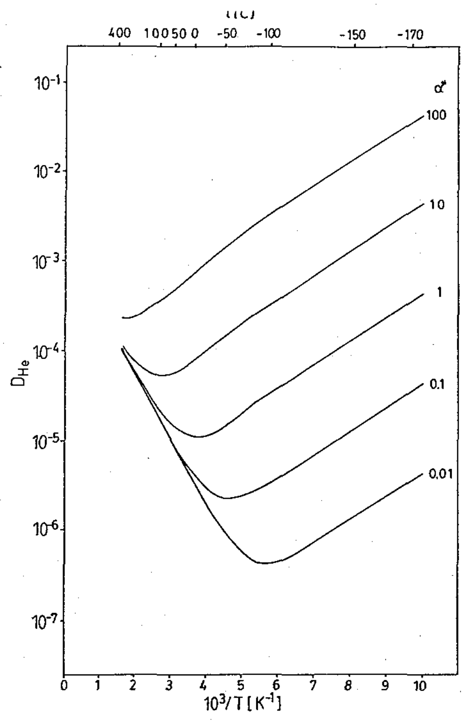

Figure 7. Apparent diffusion coefficient of He gas through a polymer membrane which has a small amount of pinholes as a function of reciprocal absolute temperature with various permeability ratios of pore flow to solution diffusion flow.

In figure 8, permeability coefficients of CH_4, N_2, O_2 and CO_2 gases through a poly(chloro-p-xylylene) membrane are plotted as a function of reciprocal temperature. The thickness of this membrane is about 5.9μm, which was prepared by vaporization and the deposited polymerization method. Measurement of permeability coeffcients as a function of feed pressure indicates that this membrane is porous. However, the permeability coefficient shows a maximum peak at 40°C, which cannot be explained by the theory presented

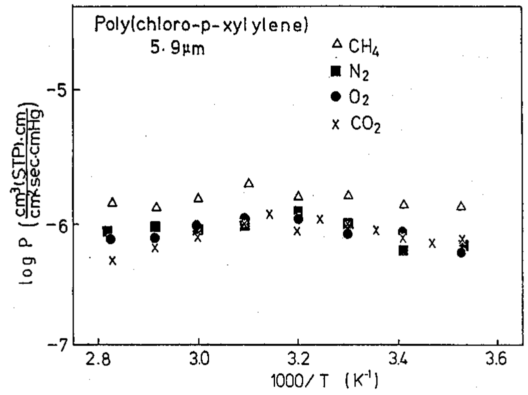

Figure 8. Permeability coefficient of CH_4, N_2, O_2 and CO_2 gas through the poly(chloro-p-xylylene) membrane whose thickness is 5.9μm, as a function of reciprocal absolute temperature.

above. Since this membrane changes its structure from temperature to temperature, it is suggested that effects of structural change are coupled with gas flows from the pores and the polymer matrix$^{8)}$.

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