Gas Transport in Rubbery Polymers

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Synopsis

Permeability coefficients have been measured for CO_2 and CH_4 in polyethylene membranes at 20, 30, and 40°C and at applied gas pressures up to ca. 2 MPa and for CH_4 in three kinds of rubber films at 25, 30, and 35°C and at applied gas pressures up to ca. 2.4 MPa. The pressure dependence of the logarithms of permeability coefficients became linear except for the CO_2–polyethylene system, where the pressure dependence became quadratic, with a minimum at a certain value of pressure. The linear and quadratic dependences can be interpreted by a free volume model of diffusion of a gas molecule in polymers. The temperature dependence of the permeability coefficients at zero pressure difference across the polymer film for each system obeyed an Arrhenius type equation.

INTRODUCTION

Gas permeation in rubbery polymers has been satisfactorily explained in terms of a solution-diffusion model controlled by the diffusion step, and the permeation rate can be usually described by simple Fick's law. In an earlier stage of the permeation studies, the permeability coefficients have been measured at relatively low pressures, not exceeding 0.1 MPa and those have been shown to be pressure-independent. However, as the measurements have been made at higher pressures, the concept of pressure independence has been found to be oversimplified. The permeability coefficients were actually found to increase or decrease as the pressure was raised above atmospheric levels.[1-3] The pressure dependence of the permeability coefficient has been interpreted in terms of a free volume model.[2,3]

In this paper, the permeabilities of methane in three kinds of rubber films and carbon dioxide and methane in a polyethylene membrane were measured for upstream pressures up to about 2.4 MPa, and compared with the free volume model. The rubber films are those utilized for the septum of oil-pressure pumps. In the oil-pressure pumps, the gas (viz., fuel gas) is separated from oil. But in a certain rubber films the gas considerably penetrates through the film into oil, gas bubbles are formed therein, and the pump finally does not work. Methane was, thus, selected as a penetrant gas. The polyethylene membrane is a typical polymer, and has been frequently used for the permeation studies.

THEORETICAL CONSIDERATIONS

The mean permeability coefficient $\overline{P}$ for isothermal transport of a penetrant gas through a nonporous membrane of thickness δ is given by

$$\overline{P} = \frac{J_s \delta}{p_h - p_1} \tag{1}$$

where J_s is the steady-state permeation flux resulting from penetrant pressures p_h and p_1 applied to the upstream and downstream surfaces, respectively. If the permeation process is controlled by a solution-diffusion mechanism, the local flux can be written in the form

$$J = -\frac{D_T}{RT}v\frac{d\mu}{dx} \tag{2}$$

where μ is the chemical potential of the penetrant gas, v is the local volume fraction of the gas in the polymer, and D_T is the thermodynamic diffusion coefficient. The chemical potential can be expressed also in terms of activity, a

$$\mu = \mu^0 + RT \ln a \tag{3}$$

so that eq. (2) becomes

$$J = -D_T\frac{\partial \ln a}{\partial \ln v}\frac{dv}{dx} \tag{4}$$

When the term $\partial \ln a / \partial \ln v$ is a constant close to unity, eq. (4) reduces to

$$J = -D_T\frac{\partial v}{\partial x} \tag{5}$$

With eq. (5), the steady-state penetrant flux is derived as

$$J_s = \frac{1}{\delta}\int_{v_1}^{v_h}D_T\,dv \tag{6}$$

where v_h and v_1 refer to the (constant) volume fractions of penetrant dissolved at upstream and downstream surfaces, respectively, being in equilibrium with pressures p_h and p_1.

According to Fujita's free-volume model,[4] the thermodynamic diffusion coefficient D_T for the diffusion of small molecules in an amorphous polymer is given by the expression

$$D_T = RTA_d\exp(-B_d/v_f) \tag{7}$$

where v_f is the volume fraction of the free volume and A_d and B_d are characteristic parameters which are thought to depend on the size and shape of the penetrant molecule, but to be independent of temperature and penetrant concentration. Kreituss and Frisch[5] extended Fujita's free-volume model to semicrystalline polymers by expressing the thermodynamic diffusion coefficient as

$$D_T = RTA_d\exp(-B_d/\phi_a v_f) \tag{8}$$

where ϕ_a refers to the amorphous volume fraction of the polymer. The fractional free volume v_f is functions of three thermodynamic variables, namely, the temperature T, the hydrostatic pressures[†] p applied on the system, and the penetrant concentration v (expressed as a volume fraction). The reference state for the free volume is taken to be as pure polymer ($v = 0$) at some reference temperature T_s and pressure p_s. Then, near this reference state, the free volume v_f can be expressed as

$$v_f = v_{fs}(T_s, p_s, 0) + \alpha(T - T_s) - \beta(p - p_s) + \gamma v \qquad (9)$$

where α $[= (\partial v_f/\partial T)_s]$ is the thermal expansion coefficient, β $[= -(\partial v_f/\partial p)_s]$ is the compressibility, and γ $[= (\partial v_f/\partial v)_s]$ is a concentration coefficient which defines the effectiveness of the penetrant as a plasticizer. The above equation can also be written in the form

$$v_f(T, p, v) = v_f^*(T) - \beta p - \gamma v \qquad (10)$$

where

$$v_f^*(T) = v_{fs}(T_s, p_s, 0) + \alpha(T - T_s) + \gamma p_s \qquad (11)$$

That is, v_f^* refers to the fractional free volume of the pure polymer at $p = 0$.
A combination of eqs. (8) and (10) leads to

$$D_T = RTA_d \exp\left(\frac{-B_d/\phi_a}{v_f^* - \beta p + \gamma v}\right) \qquad (12)$$

By substituting the above expression for D_T into eq. (6), one gets

$$J_s = \frac{RTA_d}{\delta} \int_{v_1}^{v_h} \exp\left(\frac{-B_d/\phi_a}{v_f^* - \beta p + \gamma v}\right) dv \qquad (13)$$

Substitution of eq. (13) into eq. (1) leads to the mean permeability coefficient $\overline{P}$ written as

$$\overline{P}(p_h, p_1) = \frac{RTA_d}{p_h - p_1} \int_{v_1}^{v_h} \exp\left(\frac{-B_d/\phi_a}{v_f^0 + \gamma v}\right) dv \qquad (14)$$

where

$$v_f^0 = v_f^* - \beta p_h. \qquad (15)$$

[†]p is equal to the applied penetrant pressure p_h when the membrane is rigidly supported.

When the solubility of the gas in the polymer is sufficiently low for Henry's law to hold, eq. (14) can be written in the approximate form

$$\ln \bar{P}(p_h, p_1) \cong \ln(RTA_d\bar{S}) - \frac{B_d}{\phi_a v_f^*} + \frac{B_d}{\phi_a(v_f^*)^2}\left(\gamma\bar{S} - \beta + \frac{2\beta\gamma\bar{S}p_1}{v_f^*}\right)p_1$$

$$+ \frac{B_d}{2\phi_a(v_f^*)^2}\left(\gamma\bar{S} - 2\beta + \frac{6\beta\gamma\bar{S}p_1}{v_f^*}\right)\Delta p$$

$$+ \frac{\beta\gamma\bar{S}B_d}{\phi_a(v_f^*)^3}(\Delta p)^2 \tag{16}$$

where Δp is the difference between upstream and downstream pressures ($= p_h - p_1$) and $\bar{S}$ is the mean solubility coefficient, which is defined by

$$\bar{S} = (v_h - v_1)/(p_h - p_1) \tag{17}$$

Equation (16) suggests that $\ln \bar{P}$ is expressed in the quadratic form of Δp. When the term $\beta\gamma\bar{S}B_d/\phi_a(v_f^*)^3$ is neglected as being close to zero, eq. (16) reduces to a linear equation to Δp, viz.,

$$\ln \bar{P}(p_h, p_1) = \ln(RTA_d\bar{S}) - \frac{B_d}{\phi_a v_f^*} + \frac{B_d}{\phi_a(v_f^*)^2}(\gamma\bar{S} - \beta)p_1$$

$$+ \frac{B_d}{2\phi_a(v_f^*)^2}(\gamma\bar{S} - 2\beta)\Delta p \tag{18}$$

EXPERIMENTAL

The apparatus for permeability measurements is similar to the variable volume method employed by Stern et al.[6] The gas to be permeated was fed into the high pressure side, while the low pressure side was filled with the same gas at an atmospheric pressure. The volumetric flow rate through the film to the low pressure side was measured by observing the displacement of a small amount of n-propanol in the capillary tube connected to the low pressure side. The mean permeability coefficient was determined by this steady state permeation rate. The permeation area in this cell was 19.6 cm².

Polyethylene (PE), high nitrile-content rubber (NH 5011), extremely high nitrile-content rubber (NKR 5050), and fluorine rubber (LHF) films were used as a rubbery polymer. PE film samples were provided from Toyobo Co. Ltd., Japan. NH 5011 film samples were provided from Fujikura Rubber Co., Ltd., Japan, and NKR 5050 and LHF film samples from Nikka Co., Ltd., Japan. The thickness of PE film is 56 μm and that of three kinds of rubber films is about 500 μm. Methane was used as a penetrant gas. Carbon dioxide was also used only in the case of PE films. The permeation runs in PE films were carried out at 20, 30, and 40°C and pressures up to ca. 2 MPa. Those in three
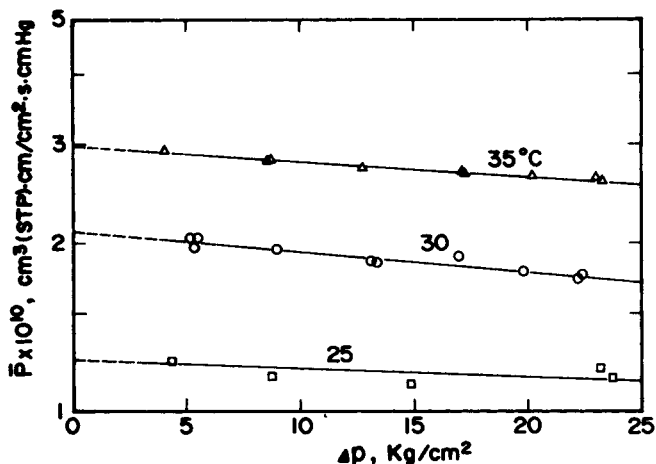
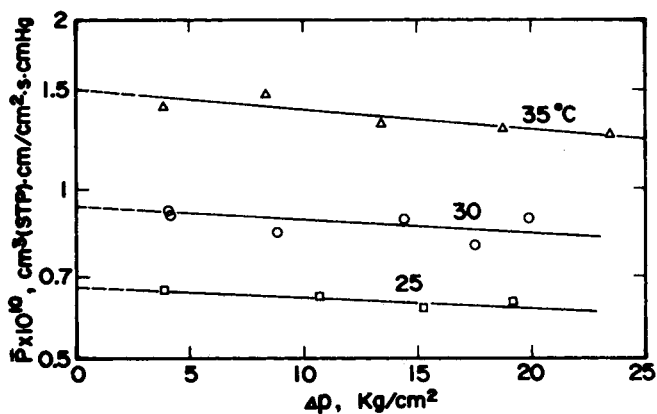Fig. 1. Dependence of permeability coefficients for methane in NH film on pressure difference.

Fig. 2. Dependence of permeability coefficients for methane in NKR film on pressure difference.

kinds of rubber films were carried out at 25, 30, and 35°C and pressures up to 2.4 MPa.

RESULTS AND DISCUSSION

The mean permeability coefficients ($\bar{P}$) at 25, 30, and 35°C were shown as a function of pressure difference across the film (Δp) on the semilogarithmic paper in Figures 1–3 for the CH_4–NH, NKR, and LHF systems, respectively. The experimental results for the CH_4– and CO_2–PE systems were illustrated also in the form of plots of log $\bar{P}$ vs. Δp for each of the temperatures investigated in Figure 4. The isothermal plots of log $\bar{P}$ vs. Δp except for the CO_2–PE system become linear. The logarithmic values of mean permeability coefficient decrease linearly with Δp for the CH_4–NH, NKR, and PE systems, whereas those for the CH_4–LHF system increase linearly with Δp. In these runs, the pressure on the low pressure side was maintained constant at
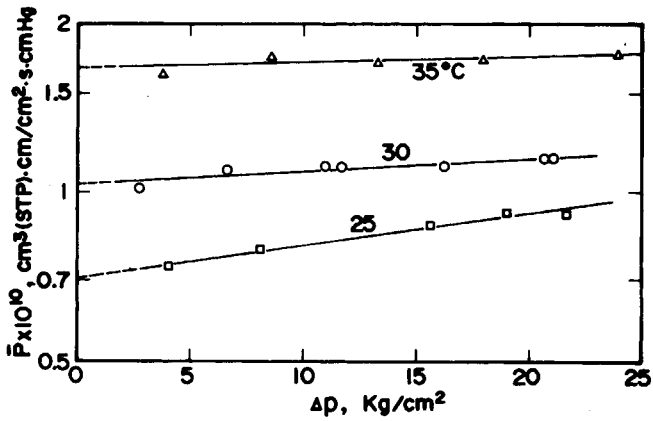
Fig. 3. Dependence of permeability coefficients for methane in LHF film on pressure difference.
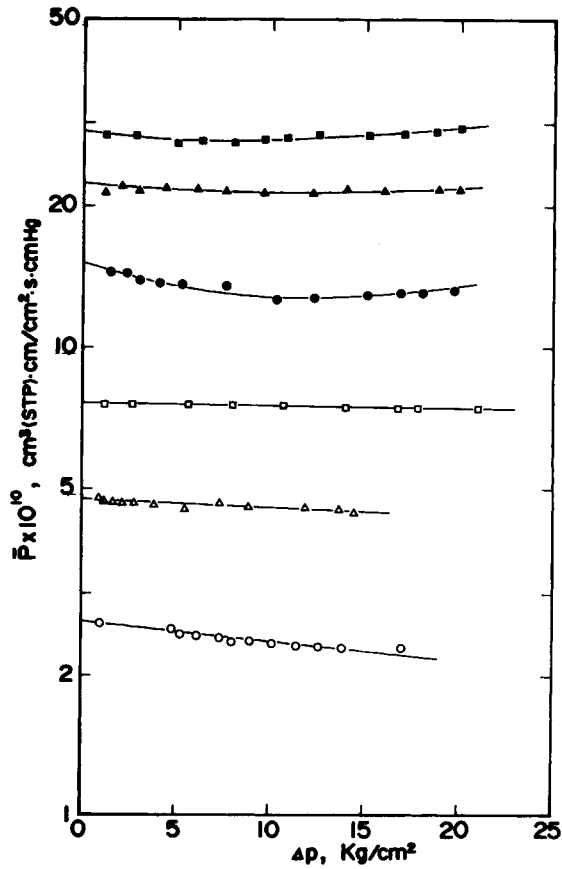

Fig. 4. Dependence of permeability coefficients for carbon dioxide and methane in polyethylene film on pressure difference. Temperatures (°C) of CH_4 ($\circ, \triangle, \square$) and CO_2 ($\bullet, \blacktriangle, \blacksquare$): ($\circ, \bullet$) 20; ($\triangle, \blacktriangle$) 30; ($\square, \blacksquare$) 40.
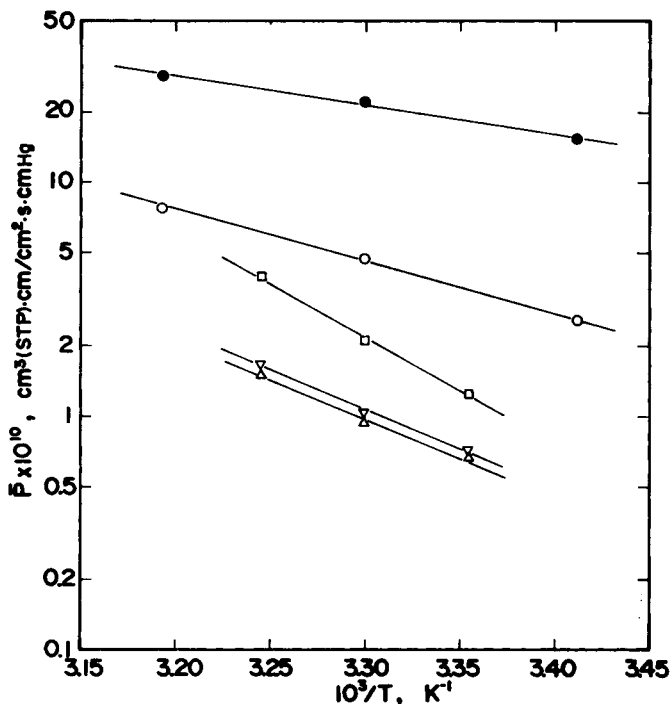
Fig. 5.   Dependence of permeability coefficients on temperature: (○) PE (CH$_4$); (●) PE (CO$_2$); (□) NH; (△) NKR; (▽) LHF.

1 atm. Therefore, such a linear dependence conforms to eq. (18). If the free volume concept is assumed to be valid, the pressure dependence of the mean permeability coefficient reflects how the free volume of the polymer is affected by pressure. An increase in the penetrant pressure on the high pressure side (in these runs) may result in two opposing effects: (1) An increase in the concentration of the penetrant dissolved in the polymer film causes an increase in the free volume. (2) A rise in the hydrostatic pressure on the high pressure side causes a decrease in the free volume. A linear decrease encountered in the cases of CH$_4$–NH, NKR, and PE systems implies that the increase in the hydrostatic pressure may cause a decrease in the free volume, while a linear increase for the CH$_4$–LHF system implies that the concentration effect of the dissolved penetrant overwhelms the hydrostatic pressure effect.

The isothermal plots of log $\bar{P}$ vs. Δp for the CO$_2$–PE system become quadratic, with a minimum at a certain pressure. Such a pressure dependence can be expected from eq. (16). At lower pressures the hydrostatic pressure effect dominates, whereas the hydrostatic pressure effect becomes overwhelmed by the concentration effect of the dissolved penetrant as the pressure on the high pressure side rises.

Figure 5 shows the Arrhenius plots of the mean permeability coefficients at the limit of zero pressure difference for each system. Good linear dependences hold for the experimental temperature ranges.

CONCLUSION

The permeability coefficients for all the systems investigated depended on the applied gas pressure. The logarithm of the permeability coefficient depends linearly on the pressure difference across the film except for the CO_2–polyethylene film system, where the dependence of the logarithm of the permeability coefficient on the pressure difference becomes quadratic, with a minimum at a certain value of pressure difference. Both linear and quadratic dependences can be represented satisfactorily in terms of a free volume model of diffusion of a gas molecule in polymers. The permeability coefficient at zero pressure difference across the film for each system showed an Arrhenius-type temperature dependence.

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