

Concentration Dependence of Diffusivities of Penetrants in Glassy Polymer Membranes

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SYNOPSIS

Steady-state permeation rates for pure CO₂, CH₄, and O₂ through two kinds of homogeneous dense membranes, copolymer of methyl methacrylate and *n*-butyl acrylate and poly(methyl methacrylate), were measured at three temperatures between 20 and 40°C and upstream pressures up to 3 MPa. The logarithms of the mean permeability coefficients for CO₂ in both membranes increased linearly or quadratically with increasing upstream pressure, whereas the mean permeabilities for CH₄ and O₂ were independent of pressure. The pressure dependence of the mean permeability coefficient for CO₂ was interpreted in terms of a modified free-volume model of diffusion for a Henry's law population in glassy polymers.

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INTRODUCTION

The dual-mode sorption and mobility model is a useful model for simulating sorption and permeation behavior in gas-glassy polymer systems. This model is based on the premise that gas molecules exist in the polymer in two distinct populations, i.e., dissolved and sorbed populations. According to the conventional dual-mode mobility model, diffusivities of the two populations are assumed to be independent of their concentrations in the polymer. However, concentration-dependent diffusivities have actually been reported for several systems.

In our previous work,^{1,2} we measured sorption equilibria and mean permeability coefficients for CO₂ in membranes of cellulose 2,4-acetate and cellulose triacetate and studied pressure dependence of the mean permeability coefficient. In such systems, the sorption equilibria could be described well by the dual-mode sorption model, whereas the pressure dependence of the mean permeability coefficient was not consistent with the corresponding dual-mode mobility model, but could, rather, be interpreted by a free-volume model,^{3,4} for the permeation of CO₂ is controlled by diffusion of dissolved population and this population has a plasticization effect on the polymer membrane. The cellulose triacetate mem-

brane was also used for studying pressure dependence of permeability coefficients for CO₂ and CH₄ in their mixture. When pure CH₄ permeated, its permeability was independent of applied pressure and therefore exhibited a constant value. In the case of the mixture, however, due to the plasticization effect of CO₂, permeabilities for CH₄ increased with increasing pressure.

In the present work, homogeneous dense membranes of a copolymer of methyl methacrylate (MMA) and *n*-butyl acrylate (BA) and of poly(methyl methacrylate) (PMMA) are used to study pressure dependence of permeability coefficients to CO₂. Mean permeability coefficients to CO₂ increased with upstream pressure. Using the present results along with the similar results of CO₂ permeation in membranes of PMMA-poly(vinylidene fluoride) (PVF₂) blends,⁵ we will discuss the concentration dependence of the diffusion coefficient of the penetrant in terms of the free-volume theory.

EXPERIMENT

The experimental apparatus and method were the same as those used in our previous work.⁶ Steady-state permeation rates were measured by the variable volume method. The downstream side of permeation cell was maintained at atmospheric pressure with pure penetrant gas. Pure CO₂, CH₄, and O₂

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were used as the penetrant gas. The membranes were 67% MMA and 33% BA (MMA-BA) copolymer produced by Kanegafuchi Chemical Co., Japan, and cast PMMA. The homogeneous dense PMMA membrane was obtained by the casting method with acetone as solvent. The concentration of PMMA in the solution was 30 wt % and the vaporization time was over 12 h.

Permeability measurements for all penetrant gases were performed on unconditioned membranes. Specifically, it should be emphasized that permeabilities to CO_2 were measured in the order of low-to-high upstream pressure. After determining the permeability at the highest upstream pressure, the membrane was changed by a new one. As the upstream pressure exceeded 2 MPa, the permeation rate of CO_2 in PMMA membrane could no longer become stable but increased with time. For this reason, the measurements for PMMA- CO_2 system were carried out at 2 MPa. Recently, Raymond and Paul indicated that permeabilities to plasticizing penetrants like CO_2 depend greatly on the experimental protocol.⁷

RESULTS

Permeability coefficients for CH_4 , O_2 , and CO_2 in commercially available copolymer membranes were plotted against a pressure difference at both sides of the membrane (Δp) in Figures 1 and 2. At each temperature, permeability coefficients for CH_4 and O_2 were found to be independent of Δp , whereas the mean permeability coefficient for CO_2 increased with

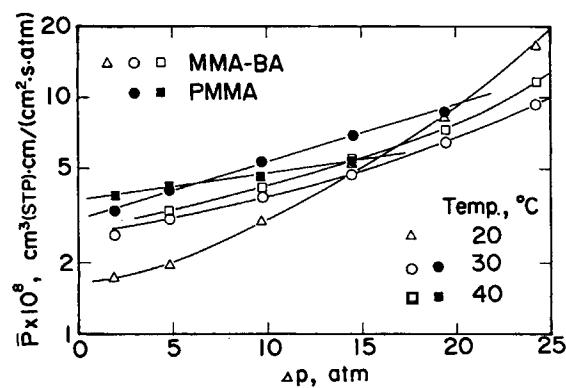


Figure 2 Pressure dependencies of mean permeability coefficients for CO_2 in MMA-BA copolymer and PMMA membranes.

increasing Δp , i.e., upstream pressure p_2 . In these figures, the permeability coefficients for CO_2 and O_2 in the cast PMMA membrane were also plotted. In comparison with the case of the copolymer, their permeability coefficients in PMMA are greater but have similar pressure dependence. The temperature dependence of the permeability coefficients for CH_4 and O_2 is shown in Figure 3. The slopes of Arrhenius plots are almost equal and the activation energy is calculated to be ca. 28 kJ/mol.

DISCUSSION

As shown in Figure 2, the mean permeability coefficients \bar{P} for CO_2 in MMA-BA copolymer mem-

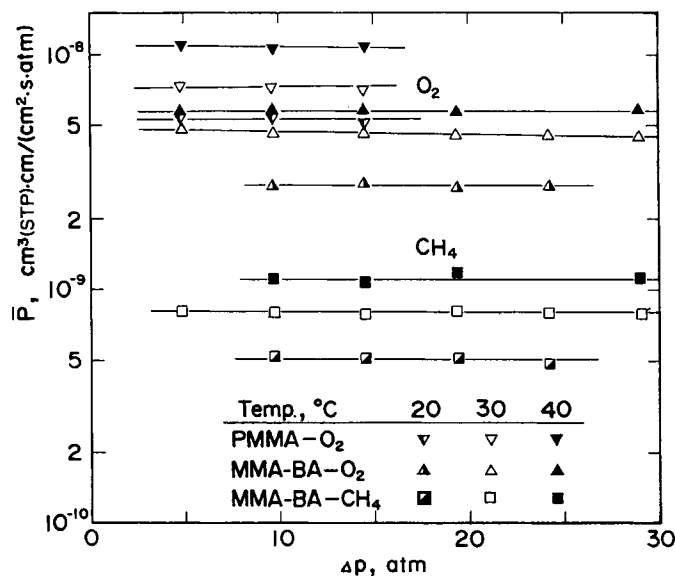


Figure 1 Permeabilities for O_2 and CH_4 in MMA-BA copolymer and PMMA membranes.

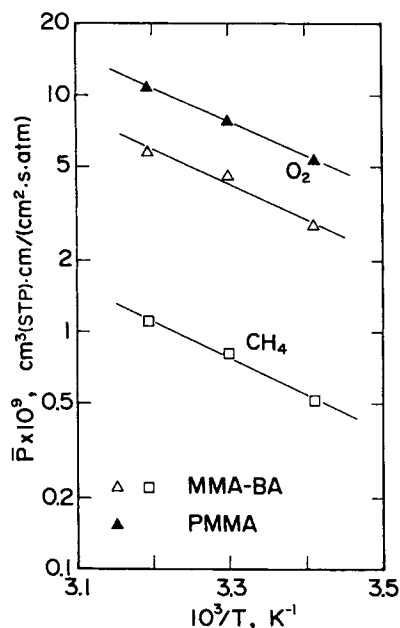


Figure 3 Temperature dependencies of permeabilities for O_2 and CH_4 in MMA-BA copolymer and PMMA membranes.

brane and PMMA membrane increase with increasing pressure difference Δp , i.e., upstream pressure p_2 . The logarithm of \bar{P} is found to be approximately a linear function of Δp in PMMA membrane and a quadratic function of Δp in MMA-BA copolymer membrane. In Figure 4, prepared by Chiou and Paul,⁵ mean permeability coefficients for CO_2 in $PVF_2/PMMA$ blends are plotted as functions of

upstream pressure. Similar pressure dependence can be seen. Only in pure PVF_2 membrane, $\log \bar{P}$ increases linearly with increasing pressure, and in PMMA and $PVF_2/PMMA$ blends, it increases quadratically with pressure. The fact that $\log \bar{P}$ increases linearly or quadratically with increasing upstream pressure indicates the applicability of the free-volume theory concerning diffusivity of the penetrant in polymer membrane.

According to the dual-sorption model, sorption of a gas in glassy polymers can be expressed as

$$C = k_D p + \frac{C'_H b p}{1 + b p} \quad (1)$$

According to the corresponding dual-mode mobility model, when the concentration gradient acts as driving force of diffusion, the mean permeability coefficient is given by

$$\bar{P} = k_D D_D + \frac{C'_H b D_H}{(1 + b p_1)(1 + b p_2)} \quad (2)$$

when D_D and D_H in eq. (2) are independent of concentrations of dissolved and sorbed populations and remain constant, the mean permeability coefficient decreases with increasing Δp or upstream pressure p_2 . However, in Figures 2 and 4, the mean permeability coefficients increase with increasing Δp or p_2 . These results obviously do not obey eq. (2). Our interpretation is that in PMMA, MMA-BA copolymer, and $PVF_2/PMMA$ membranes, the perme-

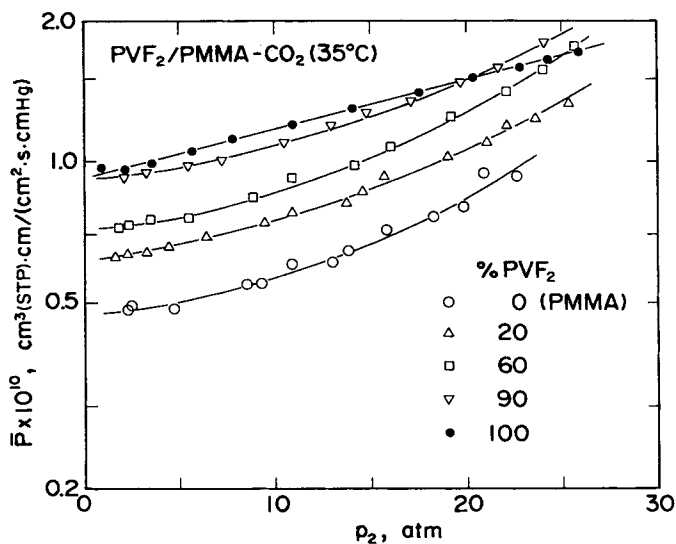


Figure 4 Pressure dependence of mean permeability coefficients for CO_2 in $PVF_2/PMMA$ blends at $35^\circ C$.

ation of CO₂ is controlled by diffusion of the dissolved population and this population exhibits a plasticization effect. Here, we use the total immobilization model ($D_H = 0$) in conjunction with the free-volume model for D_D to derive the mean permeability coefficient expression.

Thus, if the diffusion coefficient of dissolved population D_D is given by the free-volume model, viz.

$$D_D = RTA_d \exp\left(-\frac{B_d}{\phi_a v_f^*}\right) \quad (3)$$

the mean permeability coefficient can be derived as follows⁴:

$$\bar{P} = \frac{RTA_d}{p_2 - p_1} \int_{v_1}^{v_2} \exp\left(\frac{-B_d/\phi_a}{v_f^* + \gamma v}\right) dv \quad (4)$$

Expanding $(v_f^* + \gamma v)^{-1}$ in the integrand in the series and retaining the series up to the second-order term as an approximation, and integrating the resultant equation with respect to v , one obtains

$$\begin{aligned} \ln \bar{P} \cong & \ln(RTA_d \bar{S}) - \frac{B_d}{\phi_a v_f^*} \\ & + \frac{B_d}{\phi_a (v_f^*)^2} \left(\gamma \bar{S} - 2\beta + \frac{2\beta \gamma \bar{S} p_1}{v_f^*} \right) p_1 \\ & + \frac{B_d}{2\phi_a (v_f^*)^2} \left(\gamma \bar{S} - 2\beta + \frac{6\beta \gamma \bar{S} p_1}{v_f^*} \right) \Delta p \\ & + \frac{\beta \gamma \bar{S} B_d}{\phi_a (v_f^*)^3} (\Delta p)^2 \quad (5) \end{aligned}$$

In this way, $\ln \bar{P}$ can be expressed as a quadratic function of Δp . When the downstream pressure (p_1) approaches zero, $\ln \bar{P}$ becomes a quadratic function of p_2 , viz.

$$\begin{aligned} \ln \bar{P} \cong & \ln(RTA_d \bar{S}) - \frac{B_d}{\phi_a v_f^*} \\ & + \frac{B_d}{2\phi_a (v_f^*)^2} (\gamma \bar{S} - 2\beta) p_2 + \frac{\beta \gamma \bar{S} B_d}{\phi_a (v_f^*)^3} (p_2)^2 \quad (6) \end{aligned}$$

Furthermore, when the term $\beta \gamma \bar{S} B_d / \phi_a (v_f^*)^3$ approaches zero, eqs. (5) and (6) reduce to

$$\begin{aligned} \ln \bar{P} \cong & \ln(RTA_d \bar{S}) - \frac{B_d}{\phi_a v_f^*} + \frac{B_d}{\phi_a (v_f^*)^2} (\gamma \bar{S} - 2\beta) p_1 \\ & + \frac{B_d}{2\phi_a (v_f^*)^2} (\gamma \bar{S} - 2\beta) \Delta p \quad (7) \end{aligned}$$

$$\ln \bar{P} \cong \ln(RTA_d \bar{S})$$

$$- \frac{B_d}{\phi_a v_f^*} + \frac{B_d}{2\phi_a (v_f^*)^2} (\gamma \bar{S} - 2\beta) p_2 \quad (8)$$

$\ln \bar{P}$ is now a linear function of Δp or p_2 . The above formulas [eqs. (7) and (8)] agree with the approximate ones worked out by Stern et al.³

As can be seen from Figures 1, 2, and 4, the logarithms of \bar{P} for CO₂ in MMA-BA copolymer and PVF₂/PMMA blend polymer membranes increase with increasing pressure quadratically rather than linearly. Also, in PMMA membrane cast by us and PVF₂ membrane, $\log \bar{P}$ increases linearly with increasing pressure.

As shown in Figure 1, the mean permeability coefficients for O₂ and CH₄ in MMA-BA copolymer and PMMA membranes are not dependent on applied pressure. This can be explained from the viewpoint that these two gases do not have any plasticization effect on the membranes. In this case, D_D is constant and the permeability is also constant as eq. (2) with $D_H = 0$ suggests.

CONCLUSION

The mean permeability coefficients for CO₂ in homogeneous dense membranes of MMA-BA copolymer and PMMA increase with increasing upstream gas pressure. Such a pressure dependence can be described as a linear or quadratic function of the pressure and be interpreted from the viewpoint that the permeation of CO₂ is controlled mainly by diffusion of the dissolved population and, besides, this population has a plasticization effect on the membranes. By assuming that the diffusivity of the dissolved population obeys the free-volume theory, the linear and quadratic pressure dependence of the mean permeability coefficient can be explained.

NOMENCLATURE

- A_d characteristic parameter in eq. (3) (mol s/kg)
- B_d characteristic parameter in eq. (3)
- b Langmuir affinity constant (atm⁻¹)
- C total sorbed concentration [cm³(STP)/cm³]
- C_D concentration of Henry's law population [cm³(STP)/cm³]
- C_H concentration of Langmuir population [cm³(STP)/cm³]
- C'_H Langmuir capacity constant [cm³(STP)/cm³]

- D diffusion coefficient in membrane (cm^2/s)
 k_D Henry's law constant [$\text{cm}^3(\text{STP})/(\text{cm}^3 \text{ atm})$]
 \bar{P} mean permeability coefficient [$\text{cm}^3(\text{STP}) \text{ cm}/(\text{cm}^3 \text{ s atm})$] or [$\text{cm}^3(\text{STP}) \text{ cm}/(\text{cm}^2 \text{ s cmHg})$]
 p pressure of penetrant gas or hydrostatic pressure (atm)
 R gas constant [$\text{J}/(\text{mol K})$]
 \bar{S} mean solubility coefficient defined by $(v_2 - v_1)/(p_2 - p_1)$ [$\text{cm}^3(\text{STP})/(\text{cm}^3 \text{ atm})$]
 T temperature (K)
 v volume fraction concentration of penetrant gas in membrane [$\text{cm}^3(\text{STP})/\text{cm}^3$]
 $v_f = v_f(T, p, v)$, volume fraction of free volume in membrane
 $v_f^0 = v_{fs}(T_s, p_s, 0) + \alpha(T - T_s) - \beta(p - p_s)$
 $v_f^* = v_f^0 + \beta p_2$

Greek Symbols

- α thermal expansion coefficient of free volume defined by $(\partial v_f / \partial T)_s$ (K^{-1})
 β compressibility of free volume defined by $-(\partial v_f / \partial p)_s$ (atm^{-1})
 γ concentration coefficient of free volume defined by $(\partial v_f / \partial v)_s$
 Δp difference between upstream and downstream pressures (atm)
 ϕ_a amorphous volume fraction of polymer

Subscripts

- D Henry's law mode
 H Langmuir mode
 s reference state
 1 downstream surface
 2 upstream surface

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