

Permeation of Mixed Gases in Glassy Polymer Membranes

E. SADA, H. KUMAZAWA, P. XU, and S.-T. WANG,* *Department of Chemical Engineering, Kyoto University, Kyoto 606, Japan*

Synopsis

Steady-state permeation rates for pure CO₂ and CH₄ and the binary mixture through homogeneous dense polysulfone and polycarbonate membranes have been measured at 40°C and upstream pressures up to 26 atm. The pressure dependence of the mean permeability coefficients for CO₂ and CH₄ for all of the systems was simulated equally well in terms of the dual-mode mobility models driven by gradients of chemical potential and concentration. The dual-mode sorption and transport parameters used for evaluation of the mobility models are only those determined from sorption and permeation runs for a single gas. The approximate solution for the mean permeability coefficient of each component in a binary mixture was derived on the basis of the same mobility model driven by gradients of chemical potential. The deviation of approximate solutions from numerical ones remains less than 0.3%.

INTRODUCTION

Research concerning the mechanism of sorption and diffusion of gases in nonporous polymeric membranes is considered to be an essential base for development of gas separation membranes with high permselectivity. The glassy polymer is evidently one of the desirable candidates as the key material of gas separation membrane, because it should possess high thermal and chemical stabilities. The behavior of sorption and permeation for a gas in glassy polymer membranes has been found to be simulated well by so-called dual-mode sorption and mobility (transport) model. In this dual-mode model, penetrant molecules are retained in the polymer in two distinct ways, i.e., Henry's Law dissolution and Langmuir sorption. When applying the dual-mode model to the mixed gases case, one should note that the Langmuir sorption of a constituent in the mixture be influenced by the presence of the remaining constituents. Further, the mean permeability coefficient for a component in the mixture is mutually affected by the remaining constituents as is the Langmuir sorption. Though the dual-mode model has been tested in many single gas-glassy polymer systems, the applicability of the same model to the mixed gases case has been examined only in some systems.

In this paper, permeabilities for carbon dioxide and methane in the binary mixture through homogeneous dense polysulfone and polycarbonate membranes were measured to test the applicability of the dual-mode model to the binary gas mixture case. The pressure dependence of the mean permeability coefficient for each component could be described equally well by two versions of dual-

* Department of Chemical Engineering, Tianjin University, Tianjin, China.

mode mobility model using only estimates taken from sorption and permeation runs for a single gas.

EXPERIMENTAL

Pure carbon dioxide and methane and the equimolar mixture (i.e., 50 vol % CO₂ and 50 vol % CH₄) were used as a penetrant gas. Polysulfone (PSF) and polycarbonate (PC) membranes were used as a glassy polymer. PSF membrane samples (Toraylon-PS) were kindly provided by the Toray Co. (Japan). PC membrane samples were kindly supplied by the Teijin Co. (Japan). The nominal thicknesses of both PSF and PC membranes were 50 μm. The permeation cell was the same one as in our previous work¹ (permeation area = 19.6 cm²). Permeation runs were performed at 40°C and upstream total pressures up to 26 atm for pure CO₂ and CH₄ as well as binary mixture. At the downstream side, permeated gases were picked up by helium flowing at a prescribed rate. The flow rate of pickup gas was adjusted so that the partial pressure of each component might be regarded as zero. The concentrations of CO₂ and CH₄ in the downstream were determined by a gas chromatograph with a 2-m long column packed with Porapak Q. The column temperature was maintained at 50°C and helium was used as the carrier gas. The permeation rates for pure CO₂ and CH₄ runs as well as the binary mixture runs were determined from the flow rate of pickup gas and the concentrations of the components.

Sorption equilibria for CO₂ and CH₄ in the same PSF and PC membranes have been measured in our previous work^{2,3} and the dual-mode sorption parameters for all of these systems have been determined.

RESULTS AND DISCUSSION

Permeation by a Single Gas

First, the dual-mode sorption parameters appearing in

$$C = k_D p + C'_H b p / (1 + b p) \quad (1)$$

are listed in Table I for CO₂ and CH₄ in PSF and PC membranes at 40°C.

The permeability data for pure CO₂ and CH₄ in PSF and PC membranes are illustrated as functions of $b/(1 + b p_2)$ and $\ln(1 + b p_2)/p_2$ in Figures 1 and

TABLE I
Dual-Mode Sorption Parameters for CO₂ and CH₄ in PSF and PC Membranes at 40°C

Gas	Polymer	k_D [cm ³ (STP)/(cm ² atm)]	b (atm ⁻¹)	C'_H [cm ³ (STP)/cm ³]
CO ₂ (A)	PSF	0.547	0.168	18.3
CH ₄ (B)	PSF	0.413	0.0886	7.63
CO ₂ (A)	PC	0.702	0.124	16.0
CH ₄ (B)	PC	0.280	0.0872	4.72

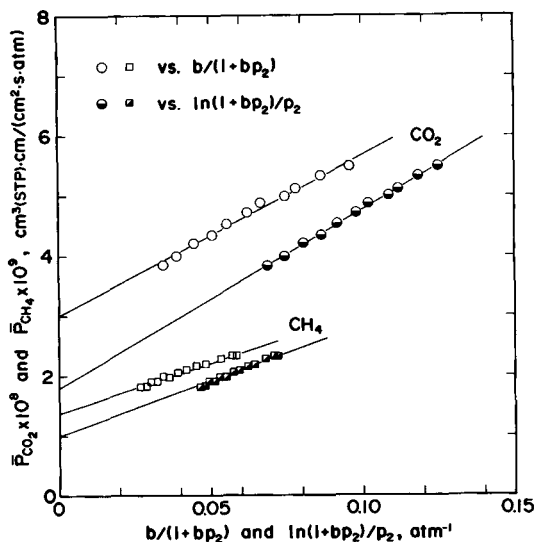


Fig. 1. Pressure dependence of mean permeability coefficients for CO_2 and CH_4 through PSF membrane at 40°C .

2, respectively. Two kinds of abscissa are employed by taking account of permeability expressions in terms of the dual-mode mobility model driven by gradients of concentration and chemical potential. That is, according to the dual-mode model driven by gradients of concentration⁴ and chemical potential,⁵ where the downstream pressure can be regarded as zero, the mean permeability coefficients are expressed as

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

$$\bar{P} = k_D D_D + C'_H D_H \ln(1 + b p_2) / p_2 \quad (3)$$

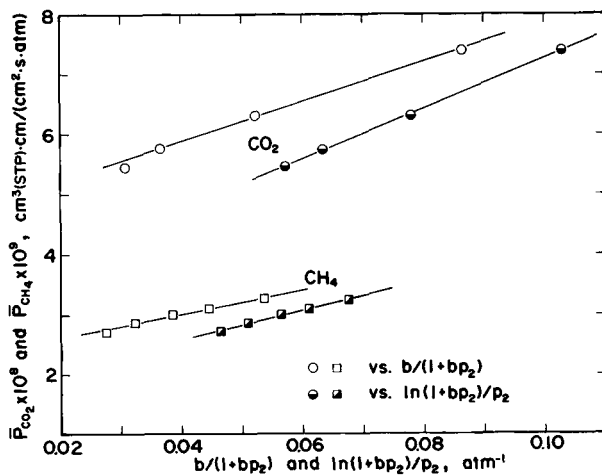


Fig. 2. Pressure dependence of mean permeability coefficients for CO_2 and CH_4 through PC membrane at 40°C .

The linearity seems rather good in the plots by eq. (2) as well as eq. (3) in view of experimental errors (maximum relative error = 1.0% for PSF and 0.9% for PC). From the intercept and slope of each straight line drawn in Figures 1 and 2, the diffusion coefficients of Henry's Law and Langmuir modes, D_D and D_H , were determined and are listed in Table II. Table II also lists the standard deviations for the dual-mode models based on both driving forces. Two versions of dual-mode model work equally well for permeation of pure CO_2 and CH_4 in PSF and PC membranes within the present experimental conditions.

Permeation by Mixed Gases

The permeability data for mixed gases will be discussed in terms of two versions of dual-mode mobility model. The dual-mode mobility model driven by gradients of concentration has been extended to the mixed gases case by Koros et al.⁶:

$$\bar{P}_A = k_{DA} D_{DA} + \frac{D_{HA} C'_{HA} b_A}{1 + b_A p_{A2} + b_B p_{B2}} \quad (4)$$

$$\bar{P}_B = k_{DB} D_{DB} + \frac{D_{HB} C'_{HB} b_B}{1 + b_A p_{A2} + b_B p_{B2}} \quad (5)$$

for a binary mixture of components A and B, but the same mobility model driven by gradients of chemical potential has not been extended to the binary mixture case yet.

When applying the dual-mode model driven by gradients of chemical potential to the case of the binary mixture of components A and B, one gets the mean permeability coefficients (Appendix A)

TABLE II
Dual-Mode Transport Parameters Derived from Plots in Figures 1 and 2
and Standard Deviations (σ) from Dual-Mode Models

Polymer	Gas	$D_D \times 10^8$ (cm^2/s)	$D_H \times 10^8$ (cm^2/s)	$\sigma \times 10^8$ [cm^3 (STP) $\text{cm}/(\text{cm}^2 \text{ s atm})$]
<u>Based on gradients of chemical potential</u>				
PSF	CO_2	3.29	1.62	0.030
PSF	CH_4	0.245	0.238	0.0034
PC	CO_2	4.27	2.67	0.032
PC	CH_4	0.550	0.534	0.0029
<u>Based on gradients of concentration</u>				
PSF	CO_2	5.48	1.45	0.065
PSF	CH_4	0.332	0.219	0.0025
PC	CO_2	6.42	2.12	0.058
PC	CH_4	0.779	0.413	0.0045

$$\bar{P}_A = k_{DA}D_{DA} + \frac{C'_{HA}b_A D_{HA}}{p_{A2} - p_{A1}} \int_1^2 \frac{dp_A}{1 + b_A p_A + b_B p_B} \quad (6)$$

$$\bar{P}_B = k_{DB}D_{DB} + \frac{C'_{HB}b_B D_{HB}}{p_{B2} - p_{B1}} \int_1^2 \frac{dp_B}{1 + b_A p_A + b_B p_B} \quad (7)$$

The ratio of steady-state flux of component A to that of component B may be equal to the molar ratio of A to B at the downstream side, so that the ratio of \bar{P}_A to \bar{P}_B must satisfy the following relation:

$$\frac{\bar{P}_A}{\bar{P}_B} = \frac{p_{A1}(p_{B2} - p_{B1})}{p_{B1}(p_{A2} - p_{A1})} \quad (8)$$

If the ratio of concentration of dissolved species of component B to that of component A is assumed to be constant everywhere in the membrane and to be equal to the ratio at the upstream surface, i.e., $C_{DB}/C_{DA} = C_{DB2}/C_{DA2} = \beta'$ as was done for gas permeation in rubbery polymer membranes by Stern et al.,⁷ then eqs. (6) and (7) are simplified to yield

$$\bar{P}_A = k_{DA}D_{DA} + \frac{C'_{HA}b_A D_{HA}}{(b_A + \beta b_B)(p_{A2} - p_{A1})} \ln \frac{1 + b_A p_{A2} + b_B p_{B2}}{1 + b_A p_{A1} + b_B p_{B1}} \quad (9)$$

$$\bar{P}_B = k_{DB}D_{DB} + \frac{\beta C'_{HB}b_B D_{HB}}{(b_A + \beta b_B)(p_{B2} - p_{B1})} \ln \frac{1 + b_A p_{A2} + b_B p_{B2}}{1 + b_A p_{A1} + b_B p_{B1}} \quad (10)$$

In the limit of zero downstream pressure, the above equations reduce to

$$\bar{P}_A = k_{DA}D_{DA} + \frac{C'_{HA}b_A D_{HA}}{(b_A + \beta b_B)p_{A2}} \ln(1 + b_A p_{A2} + b_B p_{B2}) \quad (11)$$

$$\bar{P}_B = k_{DB}D_{DB} + \frac{\beta C'_{HB}b_B D_{HB}}{(b_A + \beta b_B)p_{B2}} \ln(1 + b_A p_{A2} + b_B p_{B2}) \quad (12)$$

These are similar in form to eqs. (4) and (5) based on concentration gradients, and likewise are convenient forms for calculation.

The effect of downstream pressure on the permeability coefficients for both components will be examined on the basis of the exact solutions [eqs. (6) and (7)]. The procedure for the exact solutions is given in Appendix A. In Figure 3, the mean permeability coefficients for components A and B are indicated as functions of downstream pressure at two levels of upstream total pressure. The system to be calculated here is permeation for equimolar mixture of CO₂ and CH₄ through PSF membrane at 40°C, and the values of dual-mode sorption and transport parameters are taken from Tables I and II. It is evident that the mean permeability coefficients for both components are almost independent of downstream pressure below 0.02 atm and are equal to those in the limit of zero downstream pressure. Thus, numerical solutions for \bar{P}_A and \bar{P}_B for the sake of comparison with the corresponding experimental values were obtained for the case of downstream pressure of 0.01 atm.

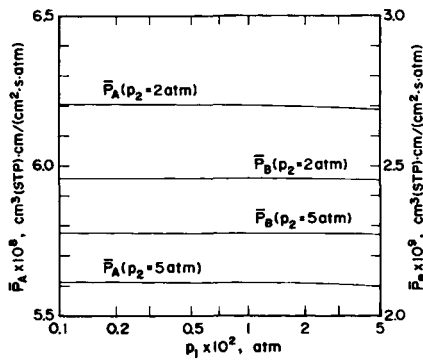


Fig. 3. Effect of downstream pressure on mean permeability coefficients for CO_2 (A) and CH_4 (B) in the binary mixture through PSF membrane at 40°C .

The experimental results on permeation for equimolar mixture of CO_2 and CH_4 through PSF and PC membranes are represented in Figure 4 (maximum relative error = 3.3% for PSF and 1.0% for PC), where the mean permeability coefficients for CO_2 and CH_4 are plotted on the basis of eqs. (11) and (12). The solid lines represent the numerical solutions for \bar{P}_A and \bar{P}_B . Only the values of dual-mode sorption and transport parameters determined from sorption and permeation runs for a single gas are used for calculation of solid lines. All of the experimental data of permeabilities are found to be in good agreement with the solid lines. The broken lines represent approximate solutions for \bar{P}_A and \bar{P}_B . The accuracy of the approximate solution is found to be very good, where the relative errors remains less than 0.3%.

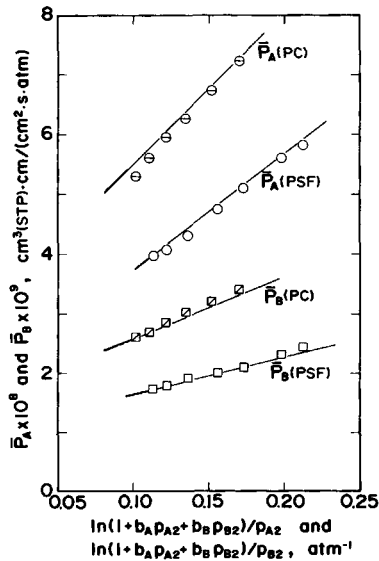


Fig. 4. Comparison of experimental values with numerical solutions in terms of dual-mode mobility model driven by gradients of chemical potential for mean permeability coefficients of CO_2 (A) and CH_4 (B) in the binary mixture through PSF and PC membranes at 40°C .

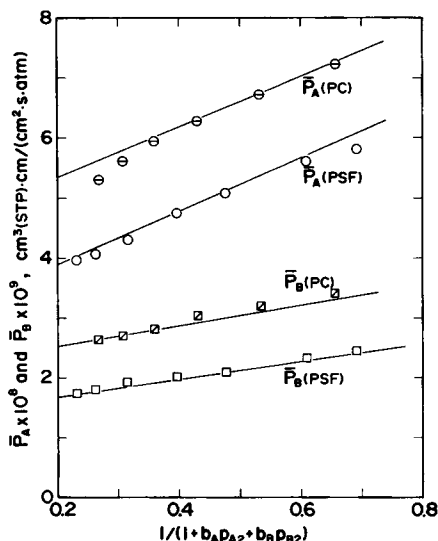


Fig. 5. Comparison of experimental values with exact solutions in terms of dual-mode mobility model driven by gradients of concentration for mean permeability coefficients of CO₂ (A) and CH₄ (B) in the binary mixture through PSF and PC membranes at 40°C.

Figure 5 shows the comparison of observed mean permeability coefficients for CO₂ and CH₄ in the equimolar mixture through PSF and PC membranes with the predictions from the dual-mode mobility model described in terms of gradients of concentration [eqs. (4) and (5)]. The permeation for the mixture can be also represented equally well by this version of dual-mode model. Table III lists the standard deviations for two versions of dual-mode model calculated in Figures 4 and 5. The standard deviations from the dual-mode model based on the chemical potential gradient are less than those from the same model based on the concentration gradient except for the system PSF-CH₄. But in view of experimental errors, it is difficult to decide whether the former version works better than the latter version.

CONCLUSION

The pressure dependence of the mean permeability coefficient for each component in the binary mixture of CO₂ and CH₄ in PSF and PC membranes could

TABLE III
Standard Deviations (σ) from Dual-Mode Models for Gas Mixture Plotted in Figures 4 and 5

Polymer	Gas	$\sigma \times 10^8$ [cm ³ (STP) cm / (cm ² s atm)], Based on Gradients of	
		Chemical potential	Concentration
PSF	CO ₂	0.085	0.125
PSF	CH ₄	0.0053	0.0050
PC	CO ₂	0.139	0.158
PC	CH ₄	0.0069	0.0088

be described equally well in terms of the dual-mode mobility model driven by gradients of chemical potential and concentration. The dual-mode sorption and transport parameters to be used for evaluation of the mobility model are only those determined from sorption and permeation runs for a single gas. Approximate solutions for the mean permeability coefficient for each component in the binary mixture were derived on the basis of the same mobility model driven by gradients of chemical potential. The maximum deviation of the approximate solution from the exact one is as small as 0.3%.

APPENDIX A

On the basis of the dual-mode mobility model driven by gradients of chemical potential, the local mass fluxes of components A and B in a planar homogeneous membrane can be written as

$$J_A = -k_{DA}D_{DA}\left(1 + \frac{F_A K_A}{1 + b_A p_A + b_B p_B}\right) \frac{dp_A}{dx} \quad (13)$$

$$J_B = -k_{DB}D_{DB}\left(1 + \frac{F_B K_B}{1 + b_A p_A + b_B p_B}\right) \frac{dp_B}{dx} \quad (14)$$

After integrating the above equations over pressure from the pressure at the downstream side to that at the upstream side with the fluxes and all coefficients constant, the mean permeability coefficients for both components can be derived as eqs. (6) and (7).

Equation (13) is divided by eq. (14) to yield the ratio of fluxes:

$$\frac{J_A}{J_B} = \frac{k_{DA}D_{DA}(1 + F_A K_A + b_A p_A + b_B p_B)}{k_{DB}D_{DB}(1 + F_B K_B + b_A p_A + b_B p_B)} \frac{dp_A}{dp_B} \quad (15)$$

The ratio of steady-state flux of component A to that of component B may be equal to the molar ratio of A to B at the downstream side, so that eq. (15) is written as

$$\frac{p_{A1}}{p_{B1}} = \frac{k_{DA}D_{DA}(1 + F_A K_A + b_A p_A + b_B p_B)}{k_{DB}D_{DB}(1 + F_B K_B + b_A p_A + b_B p_B)} \frac{dp_A}{dp_B} \quad (16)$$

To evaluate the mean permeability coefficients for components A and B, the values of partial pressures of these components at the downstream side should be known. Equation (16) can be used to find the partial pressures of A and B at the downstream side where the sum of partial pressures of these components is known. The procedure is as follows:

1. Assume the partial pressure of component A at the downstream side, p_{A1} . Then, the partial pressure of component B, p_{B1} , is also known.
2. Integrate eq. (16) with respect to p_B from p_{B1} to p_{B2} numerically by means of the Runge-Kutta-Gill method. Then, the profile of pressure of component A over the range from p_{A1} to p_{A2} is given as a function of p_B .
3. Compare the value of p_{A2} obtained thus with the prescribed value. The steps (1)–(3) are repeated until the desired agreement between calculated and prescribed values of p_{A2} is achieved.
4. After a reasonable value of p_{A2} has been reached and the relation of p_A to p_B ranging from downstream to upstream has been established, the mean permeability coefficients for components A and B are finally calculated by eqs. (6) and (7), respectively.

APPENDIX B: NOMENCLATURE

b	Langmuir affinity constant (atm^{-1})
C'_H	Langmuir capacity constant [$\text{cm}^3(\text{STP})/\text{cm}^3$]
D	diffusion coefficient in polymer phase (cm^2/s)
F	mobility ratio defined by D_H/D_D
J	diffusion flux [$\text{cm}^3(\text{STP})/(\text{cm}^2 \text{ s})$]
K	$C'_H b/k_D$
k_D	Henry's law constant [$\text{cm}^3(\text{STP})/(\text{cm}^3 \text{ atm})$]
\bar{P}	mean permeability coefficient [$\text{cm}^3(\text{STP}) \text{ cm}/(\text{cm}^2 \text{ s atm})$]
p	pressure (atm)
p_I	partial pressure of component I ($I = \text{A, B}$) (atm)
x	distance coordinate (cm)
β	p_{B2}/p_{A2} ($= k_{DA}\beta'/k_{DB}$)
β'	C_{DB}/C_{DA} ($= C_{DB2}/C_{DA2}$)
σ	standard deviation in mean permeability coefficient [$\text{cm}^3(\text{STP}) \text{ cm}/(\text{cm}^2 \text{ s atm})$]

Subscripts

A	component A (CO_2)
B	component B (CH_4)
D	Henry's Law mode
H	Langmuir mode
1	downstream side
2	upstream side

References

1. E. Sada, H. Kumazawa, and P. Xu, *J. Appl. Polym. Sci.*, **35**, 1497 (1988).
2. E. Sada, H. Kumazawa, H. Yakushiji, Y. Bamba, K. Sakata, and S.-T. Wang, *Ind. Eng. Chem. Res.*, **26**, 433 (1987).
3. E. Sada, H. Kumazawa, P. Xu, and M. Nishigaki, *J. Membr. Sci.*, **37**, 165 (1988).
4. D. R. Paul and W. J. Koros, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 675 (1976).
5. J. H. Petropoulos, *J. Polym. Sci. Polym. Phys. Ed.*, **8**, 1797 (1970).
6. W. J. Koros, R. T. Chern, V. Stannett, and H. B. Hopfenberg, *J. Polym. Sci. Polym. Phys. Ed.*, **19**, 1513 (1981).
7. S. A. Stern, G. R. Mauze, and H. L. Frisch, *J. Polym. Sci. Polym. Phys. Ed.*, **21**, 1275 (1983).

Received February 1, 1989

Accepted June 9, 1989