Korean J. of Chem. Eng., **10**(1), 44-48 (1993)

GAS PERMEATION THROUGH GLASSY POLYMER MEMBRANES WITH RELATIVELY LOW GLASS-TRANSITION TEMPERATURE

Seong-Youl Bae, Du-Hyon Cho, Sang-Wook Ko, Hee-Taik Kim and Hidehiro Kumazawa***

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea
*Department of Chemical Engineering, Kyoto University, Kyoto, Japan

(*Received 19 September 1992 • accepted 30 November 1992*)

Abstract—When the glass-transition temperature of the polymer is not so much higher than the experimental temperature, the pressure dependence of the mean permeability coefficient of the polymer membrane to a gas is apt to deviate from the prediction by the conventional dual-mode mobility model, and to obey a similar model with concentration-dependent diffusivities because of the plasticization action of sorbed gas in the polymer membrane. In this work, sorption and permeation for oxygen and carbon dioxide in a membrane of polystyrene whose glass-transition temperature is 95℃, were measured to discuss the mechanism of gas diffusion in glassy polymer membranes with relatively low glass-transition temperature at 30, 40 and 50℃ respectively.

INTRODUCTION

The sorption of gases and vapors in glassy polymers is generally more complex than in rubbery polymers. The sorption equilibria of gases in glassy polymers have been measured for many gas-glassy polymer systems, and have been described well in terms of a so-called dual-mode sorption model. In the dual-mode sorption model, sorbed molecules are retained in the polymer in two distinct ways, i.e. via Henry's law dissolution and Langmuir-type adsorption. Currently, it is no exaggeration to say that this dual-mode concept at sorption equilibrium has been well established. The two sorbed populations, which are termed Henry's law and Langmuir populations, respectively, can execute diffusive movements with different mobilities while being at local equilibrium with each other. This parallel approach called dual-mode mobility model, has not been tested in many gas-glassy polymer systems, as opposed to the dual-mode sorption model, and the applicability of this model has not been confirmed yet.

When the temperature in permeation runs is much lower than the glass-transition temperature (T_g), that is, T_g of the polymer membrane is very high as compared to the experimental temperature, the pressure dependence of the mean permeability coefficient to CO_2 is apt to deviate from the prediction by the conventional dual-mode mobility model, and to be predicted by the modified dual-mode mobility model. This modified mobility model is based on the premise that two kinds of population (i.e. Henry's law and Langmuir population) undergo diffusive movements with these two respective modes and besides, execute jumps between the two modes. This has already been met in systems of CO_2-polyimide (T_g=285℃) [1], CO_2, CH_4-polysulfone (T_g=190℃) [2], and CO_2-poly etherimide (T_g=216℃) [3].

On the other hand, when the experimental temperature is not so much lower than T_g of the polymer, also, the pressure dependence of the mean permeability coefficient is apt to deviate from the prediction by the conventional dual-mode mobility model, and to obey a dual-mode mobility model with concentration-dependent diffusivities proposed by Zhoh and Stern [4]. This case has been met in the systems of CO_2-cellulosetriacetate and CO_2-methylmethacrylate-n-butyl-acrylate copolymer [5]. The pressure dependence of diffusivities of Henry's law an Langmuir populations can be regarded as the result of the plasticization action of sorbed CO_2 in the polymer membrane.

By considering these, sorption and permeation for O_2 and CO_2 in polystyrene membrane whose glass-transition temperature is 95℃, were measured to discuss

---

**To whom all correspondence should be addressed.

more the mechanism of gas diffusion in glassy polymer membranes with relatively low glass-transition temperature.

EXPERIMENTAL

Equilibrium sorption of a gas by a polymer film sample was measured by the a pressure decay method. The pressure in the sorption cell was continuously measured by a pressure transducer.

Permeabilities for a pure gas was measured by a variable volume method. Here, permeation rates for a gas were determined by observing the displacement of a small amount of water in the capillary tube connected to the downstream pressure side maintained at one atmospheric pressure by the same penetrant gas. The permeability for a gas was calculated from the steady-state permeation rate. The permeation area in the cell is 19.6 cm².

Oxygen and carbon dioxide were used as a penetrant gas or sorbate, and polystyrene (PS) films were used as a glassy polymer with a relatively low glass-transition temperature (95℃). PS film samples were provided by Mitsubishi-Monsanto Chemical Co. Ltd., Japan. Sorption and permeation runs were carried out at 30, 40 and 50℃ and upstream pressure up to 25 atm.

RESULTS AND DISCUSSION

1. Sorption Equilibria

The measured sorption isotherms for O_2 and CO_2 in a homogeneous membrane at 30, 40 and 50℃ are presented in Fig. 1. Every isotherm exhibits a similar downward concave pattern, characteristic of glassy polymers. The sorption behavior for O_2 and CO_2 can be simulated well by the dual-mode sorption model, viz.

$$C = C_D + C_H = k_D p + \frac{C_H' bp}{1+bp} \tag{1}$$

The values of the dual-mode sorption parameters, k_D, b and C_H' were estimated by the Marquardt method [6]. and are listed Table 1. The solid curves in Fig. 1 represent the calculated sorption isotherms by Eq. (1) using these estimates. The temperature dependences of k_D and b for both gases are shown as van't Hoff plots in Fig. 2. The variation of C_H' with temperature is the plotted in Fig. 3.

2. Permeabilities to O_2

The mean permeability coefficients for O_2 in PS membrane at temperature covered here exhibited pressure dependence, that is, they decreased with increasing upstream pressure, as encountered in glassy polymer membranes. Fig. 4 shows the pressure dependence of the mean permeability coefficients on the basis of a dual-mode mobility model driven by gradients of concentration [7], viz.

$$\bar{P} = k_D D_D + \frac{bC_H' D_H}{(1+bp_1)(1+bp_2)} \tag{2}$$

It is apparent from this figure that the pressure dependences of the permeabilites here approximately follow linear relationship, and hence the conventional dual-mode mobility model (where both diffusivities of Henry's law and Langmuir polulations, D_D and D_H, are assumed to be constant) works well at these temperature. From the intercept and slope of each straight line, the diffusion coefficients D_D and D_H can be deter-

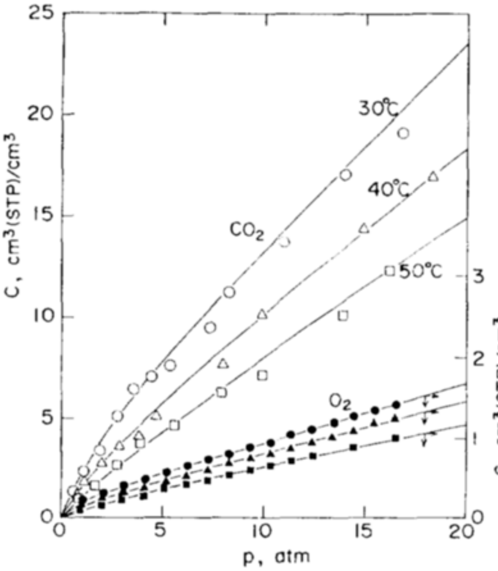

Fig. 1. Sorption isotherms for O_2 and CO_2 in PS membrane.

Table I. Dual-mode sorption parameters for O_2 and CO_2 in polystyrene membrane

Gas	Temp. [℃]	k_D [cm³(STP)/(cm³ atm)]	b [atm⁻¹]	C_H' [cm³(STP)/cm³]
O_2	30	0.074	1.22	0.22
O_2	40	0.066	0.80	0.16
O_2	50	0.053	0.50	0.13
CO_2	30	1.00	0.52	3.95
CO_2	40	0.78	0.34	3.10
CO_2	50	0.68	0.25	1.70

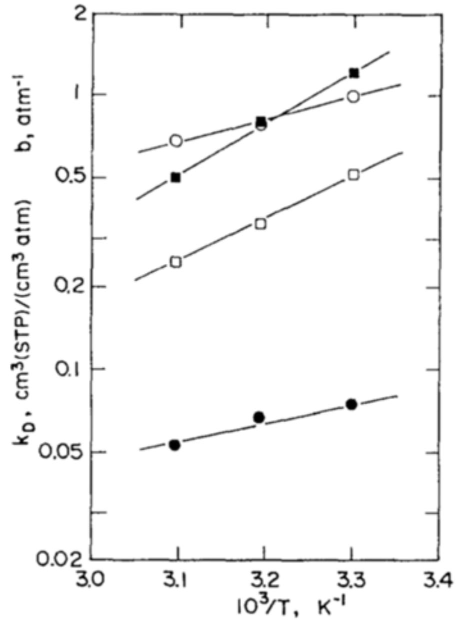

Fig. 2. Temperature dependences of Henry's law constant (circles) and Langmuir capacity constant (squares) for O_2 (full symbols) and CO_2 (open symbols) in PS.

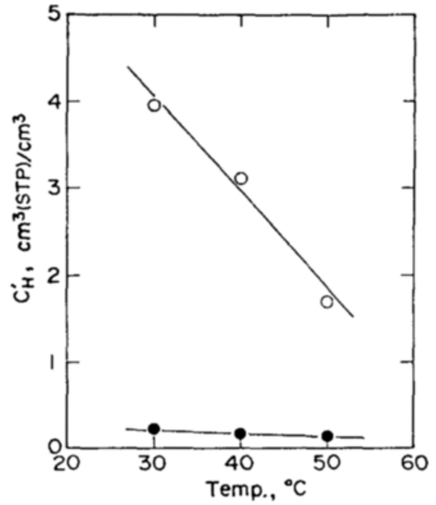

Fig. 3. Langmuir capacity constants for O_2 (full circles) and CO_2 (open circles) in PS as a function of temperature.

mined, respectively. They are listed in Table 2. The temperature dependence of these two diffusivities are shown as Arrhenius plots as full symbols in Fig. 5.

3. Permeabilities to CO_2

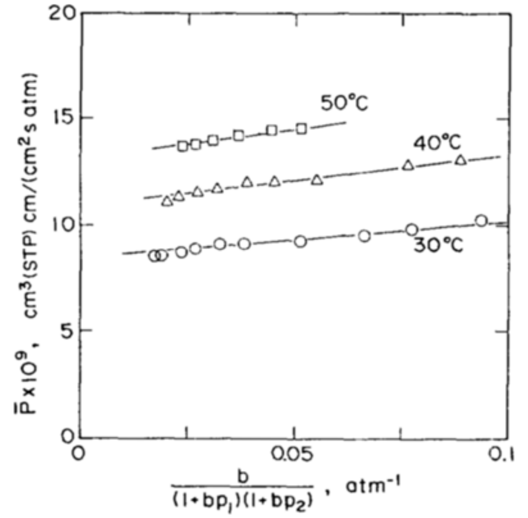

Fig. 4. Pressure dependence of mean permeability coefficients for O_2 in PS on the basis of a dual-mode mobility model.

Table 2. Diffusion coefficients in a dual-mode mobility model for O_2-PS

Temp. [℃]	$D_D \times 10^7$ [cm^2/s]	$D_H \times 10^7$ [cm^2/s]
30	1.12	0.891
40	1.65	1.44
50	2.47	2.17

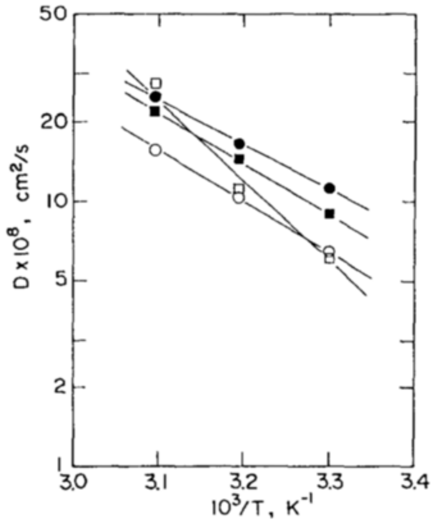

Fig. 5. Temperature dependences of diffusivities of Henry's law (circles) and Langmuir (squares) modes in a dual-mode mobility model for O_2 (full symbols) and CO_2 (open symbols) in PS.

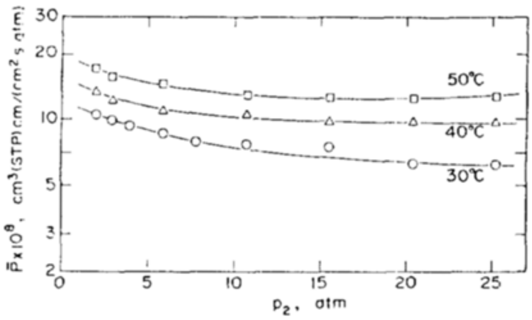

Fig. 6. Mean permeability coefficients for CO_2 in PS membrane as a function of upstream pressure.

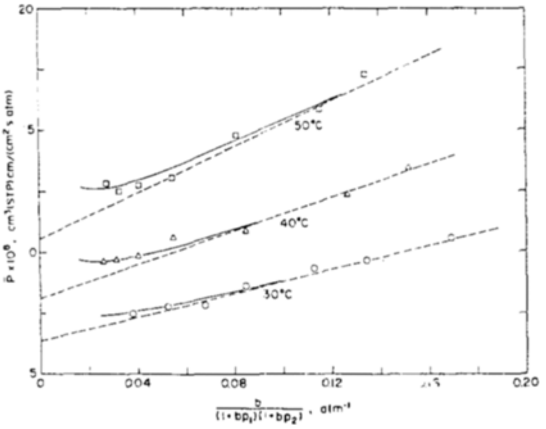

Fig. 7. Pressure dependence of mean permeability coefficients for CO_2 in PS.

The mean permeability coefficients for CO_2 at 30, 40 and 50℃ were presented as a function of upstream pressure in Fig. 6. The permeabilites at 30 and 40℃ decreased with increasing upstream pressure, whereas at 50℃ it decreased in a low pressure region and afterward increased slightly with an increase in upstream pressure. The mean permeability coefficient data were plotted on the basis of Eq. (2) in Fig. 7. The plots deviated considerably from straight lines specifically in the high upstream pressure region. That is, the permeabilities at relatively high upstream pressures deviate upward from the conventional dual-mode mobility model predictions represented by broken lines. Such an upward deviation may be arisen from the plasticization action of sorbed CO_2. Zhou and Stern [4] proposed a modified dual-mode mobility model wherein diffusivities of dissolved and adsorbed polulations depend on the concentrations of the corresponding populations:

$$D_D = D_{D0}\ \exp(\beta_D C_D) \tag{3}$$

Table 3. Diffusion coefficients in a modified dual-mode mobility model for CO_2-PS

Temp. [℃]	$D_{D0}\times10^7$ [cm²/s]	$D_{H0}\times10^7$ [cm²/s]	β* [cm³/cm³(STP)]
30	0.640	0.610	0.005
40	1.05	1.11	0.007
50	1.55	2.77	0.008

*assumed $\beta_D = \beta_H = \beta$

$$D_H = D_{H0}\ \exp(\beta_H C_H) \tag{4}$$

where β_D and β_H refer to parameters representing the plasticization action induced by dissolved and adsorbed species, respectively. The mean permeability coefficient can be derived as follows [5]:

$$\bar{P} = \frac{D_{D0}}{\beta_D(p_2 - p_1)}\left[\exp(\beta_D C_{D2}) - \exp(\beta_D C_{D1})\right] + \frac{D_{H0}}{\beta_H(p_2 - p_1)}\left[\exp(\beta_H C_{H2}) - \exp(\beta_H C_{H1})\right] \tag{5}$$

The permeability data for CO_2 plotted in Fig. 7 will be fitted to Eq. (5). From the intercept and slope of each broken line, which conforms to permeability data at low upstream pressures, D_{D0} and D_{H0} can be determined. The values of these diffusivities at each temperature are listed in Table 3. From the comparison of permeability data at high pressures with Eq. (5), β_D and β_H can be evaluated. Here, by assuming that $\beta_D = \beta_H (= \beta)$, the optimum values of β at every temperature was determined, and are listed in Table 3. The solid curves represent calculated results by Eq. (5) with these estimates.

CONCLUSION

Sorption behavior for O_2 and CO_2 in polystyrene membrane with a relatively low glass-transition temperature (95℃) at 30, 40 and 50℃ can be described well by a dual-mode sorption model. The pressure dependences of mean permeability coefficients for O_2 in the same temperature range obey a conventional dual-mode mobility model, whereas those for CO_2 are simulated better by a modified dual-mode mobility model wherein diffusivities of Henry's law and Langmuir species depend on the concentrations of respective species.

NOMENCLATURE

b : Langmuir affinity constant [atm⁻¹]
C : total sorbed concentration [cm³(STP)/cm³]
C_D : concentration of Henry's law population [cm³

(STP)/cm^3]
C_H : concentration of Langmuir population [cm^3(STP)/cm^3]
C_H' : Langmuir capacity constant [cm^3(STP)/cm^3]
D : diffusion coefficient in membrane [cm^2/s]
k_D : Henry's law constant [cm^3(STP)/(cm$^3\cdot$atm)]
$\bar{P}$: mean permeability coefficient [cm^3(STP)$\cdot$cm/(cm$^2\cdot$s$\cdot$atm)]
p : pressure of penetrant gas [atm]
β : concentration-dependence parameter appearing in Eqs. (3) and (4) [cm^3/cm^3(STP)]

Subscripts

D : Henry's law mode
H : Langmuir mode
0 : zero concentration state
1 : downstream surface
2 : upstream surface

REFERENCES

1. Sada, E., Kumazawa, H. and Xu, P.: *J. Appl. Polym. Sci.*, **35**, 1497 (1988).
2. Sada, E., Kumazawa, H., Xu, P. and Nishigaki, M.: *J. Membrane Sci.*, **37**, 165 (1988).
3. Kumazawa, H., Wang, J. S., Fukuda, T. and Sada, E.: *J. Membrane Sci.*, in press.
4. Zhou, S. and Stern, S. A.: *J. Polym. Sci.: Part B: Polym. Phys.*, **27**, 205 (1989).
5. Sada, E., Kumazawa, H. and Wang, J. S.: *J. Polym. Sci.: Part B: Polym. Phys.*, **30**, 105 (1992).
6. Marquardt, D. W.: *J. Soc. Industr. Math.*, **11**, 2 (1963).
7. Paul, D. R. and Koros, W. J.: *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 675 (1976).