Korean J. of Chem. Eng., **11**(2), 127-130 (1994)

NOTE

TRANSPORT OF OXYGEN AND CARBON DIOXIDE THROUGH POLYCARBONATE MEMBRANE

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

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea
*Department of Chemical Engineering, Kyoto University, Kyoto 606-01, Japan

(*Received 15 April 1993 • accepted 4 November 1993*)

Abstract—Sorption equilibria and permeation rates for oxygen and carbon dioxide in polycarbonate membrane were measured at different temperature between 30 and 60℃ and at pressures up to 2.5 MPa. The pressure dependence of mean permeability coefficient to oxygen obeyed the conventional dual-mode mobility model, whereas that to carbon dioxide followed a modified dual-mode mobility model with concentration-dependent diffusivities, as that of polystyrene to the same gas did.

INTRODUCTION

The sorption and diffusion of a gas in glassy polymer membranes generally follow the dual-mode model. Specifically, the dual-mode sorption model has been well established, whereas the dual-mode mobility model has not been examined in many gas-glassy polymer systems. Recently, some deviation from this mobility model has been reported. For example, when the temperature for permeation runs is not so much lower than the glass-transition temperature (T_g), 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 Zhou and Stern [1]. This case was met in the systems of CO_2-cellulose triacetate and CO_2-methylmethacrylate-n-butyl acrylate copolymer [2]. In our proceeding work, also the pressure dependence of the mean permeability coefficient for CO_2 in polystyrene membrane (T_g=95℃) was interpreted in terms of such a modified dual-mode mobility model [3].

The present work was undertaken to check the applicability of the modified dual-mode mobility model to the system of CO_2-polycarbonate membrane whose glass-transition temperature is 140℃.

EXPERIMENTAL

Oxygen and carbon dioxide were used as a penetrant gas or sorbate, and homogeneous polycarbonate (PC) membranes were used as a glassy polymer film. PC film samples were kindly provided from Teijin Co., Ltd., Japan. Sorption equilibria for a gas in that membrane at different temperatures were measured by a pressure decay method [3]. The pressure in the sorption cell was continuously detected by a pressure transducer. Sorption runs were carried out at temperatures of 30℃, 40℃, 50℃, and 60℃ and pressures up to 1.7 MPa.

The permeation rates for a pure gas were measured by means of a variable volume method [3]. Here, the permeation rates were determined by observing the displacement of a small amount water in the capillary tube connected to the downstream pressure side maintained at an atmospheric pressure by the same penetrant gas. The mean permeability coefficient to a gas was calculated from steady-state permeation rate, permeation area of the cell (19.6 cm^2), difference between upstream and downstream pressures of penetrant gas and thickness of membrane, viz. $\bar{P}=J_s\delta/\Delta p$. Permeation runs for oxygen were carried out at temperatures of 30℃, 40℃, 50℃ and 60℃ and upstream pressures up to 2.5 MPa, and those for carbon dioxide were performed at temperatures of 30℃, 40℃ and 50℃ and upstream pressures up to 2.5 MPa.

RESULTS AND DISCUSSION

1. Sorption Equilibria

The measured sorption isotherms for O_2 and CO_2 in a homogeneous membrane of PC at various temperatures range from 30℃ to 60℃ are shown in Figures

---

**To whom correspondence should be addressed.

Table 1. Dual-mode sorption and mobility parameters for O_2 in PC membrane at 30°C, 40°C, 50°C and 60°C

Temp. [°C]	$k_D\times10^6$ [m^3 (STP)/(m^3 Pa)]	$b\times10^6$ [Pa^{-1}]	C_H' [m^3 (STP)/m^3]	$D_D\times10^{11}$ [m^2/s]	$D_H\times10^{11}$ [m^2/s]	F ($=D_H/D_D$)
30	0.780	13.10	0.84	0.767	0.160	0.21
40	0.494	7.90	0.78	1.470	0.253	0.17
50	0.296	3.95	0.60	2.920	0.407	0.14
60	0.178	1.97	0.25	6.240	1.180	0.19

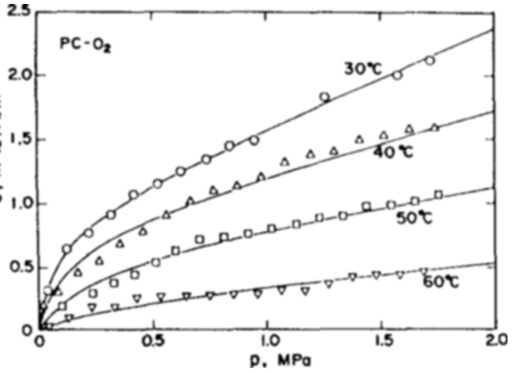

Fig. 1. Sorption isotherms for O_2 in PC at 30°C, 40°C, 50°C and 60°C.

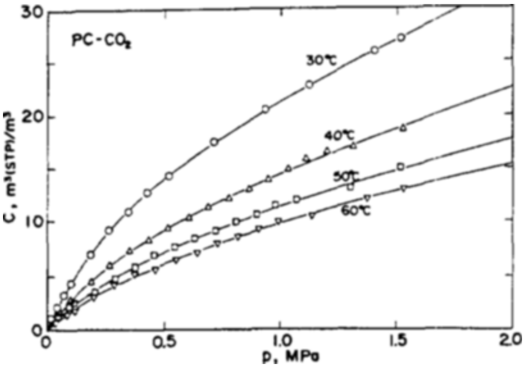

Fig. 2. Sorption isotherms for CO_2 in PC at 30°C, 40°C, 50°C and 60°C.

Table 2. Dual-mode sorption parameters for CO_2 in PC at 30°C, 40°C, 50°C and 60°C

Temp. [°C]	$k_D\times10^6$ [m^3 (STP)/(m^3 Pa)]	$b\times10^6$ [Pa^{-1}]	C_H' [m^3 (STP)/m^3]
30	8.79	2.35	17.70
40	6.72	2.22	11.11
50	5.17	2.01	9.20
60	4.38	1.73	8.52

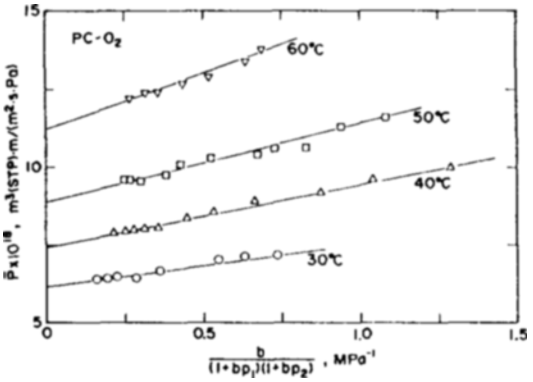

Fig. 3. Pressure dependences of mean permeability coefficients for O_2 in PC membrane at 30°C, 40°C, 50°C and 60°C.

1 and 2, respectively. The isotherms for both gases at each temperature exhibit nonlinear patterns similar to those obtained for other glassy polymers [3, 4]. Likewise, the sorption behavior could be adequately described in terms of the dual-mode sorption model, viz.

$$C=C_D+C_H=k_DP+\frac{C_H'bP}{1+bP} \qquad (1)$$

The values of the dual-mode sorption parameters, k_D, b, and C_H' for O_2 and CO_2 were determined by the Maquardt method [5], and are listed in Tables 1 and 2, respectively. All of solid curves in Figures 1 and 2 represent the sorption isotherms calculated using Eq. (1) and there estimated values.

2. Permeabilities to O_2

The mean permeability coefficients for O_2 in PC membrane at 30°C , 40°C , 50°C and 60°C were exhibited pressure dependence definitely. At every temperature, the mean permeability coefficients decreased with increasing upstream pressure. Such a pressure dependence seems to be characteristic of glassy polymer membranes. It was checked whether a dual-mode mobility model driven by gradients of concentration worked or not. Figure 3 shows the pressure dependence of the mean permeability coefficient on the basis of the dual-mode mobility model, viz.

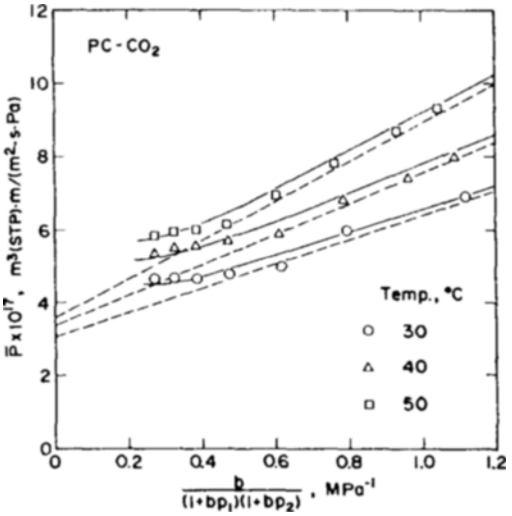

Fig. 4. Pressure dependences of mean permeability coefficients for CO_2 in PC membrane at 30°C, 40°C and 50°C. The full curves represent the calculated results by a modified dual-mode model, while the broken lines represent the calculated results by a conventional dual-mode model.

$$P = k_D D_D + \frac{bC_H' D_H}{(1+bP_1)(1+bP_2)} \quad (2)$$

The plot in terms of Eq. (2) gave essentially straight lines. It implies that the dual-mode mobility model is applicable to this system. From the slop and intercept of each line, the values of diffusivities, D_D and D_H, were determined, and are listed in Table 1. It should be noted in Eq. (2), i.e., conventional dual-mode mobility model, both diffusivities of Henry's law and Langmuir populations, D_D and D_H, are assumed to be constant.

3. Permeabilities to CO_2

The permeability data for CO_2 in PC membrane at 30, 40 and 50C were plotted also on the basis of Eq. (2) in Figure 4. The plots, however, are not on straight line at all. The permeabilites at relatively high upstream pressures deviate upward from the conventional dual-mode mobility model predictions represented by broken lines. Such an upward deviation has been observed in the permeation for the same gas (CO_2) in polystyrene membrane [3], where the deviation has been interpreted by a plasticization action of sorbed CO_2. According to a modified dual-mode mobility model proposed by Zhou and Stern [1], the mean permeability coefficient can be written as

Table 3. Estimated values for diffusion coefficients of Henry's Law and Langmuir populations in the limit of zero concentration and plasticization parameter (β) for CO_2 in PC membrane at various temperatures

Temp. [°C]	$D_{D0}\times10^{12}$ [m²/s]	$D_{H0}\times10^{12}$ [m²/s]	F (=D_{H0}/D_{D0})	β [m³ (STP)/m³]
30	3.50	1.85	0.53	0.010
40	5.00	3.77	0.75	0.018
50	6.96	5.76	0.83	0.021

$\beta_D = \beta_H = \beta$ assumed

$$P = \frac{D_{D0}}{\beta_D(P_2-P_1)}[\exp(\beta_D C_{D_2}) - \exp(\beta_D C_{D_1})] + \frac{D_{H0}}{\beta_H(P_2-P_1)}[\exp(\beta_H C_{H_2}) - \exp(\beta_H C_{H_1})] \quad (3)$$

where D_{D0} and D_{H0} refer to diffusivities of dissolved and adsorbed species, respectively, in the limit of zero respective concentration, and β_D and β_H designate parameters representing the plasticization action induced by dissolved and adsorbed species, respectively. It should be remembered that the diffusivities of respective species are given as

$$D_D = D_{D0} \exp(\beta_D C_D) \quad (4)$$

$$D_D = D_{H0} \exp(\beta_H C_H) \quad (5)$$

In the present case, the plasticization effect did not appear so much, because the sorption equilibria were not influenced by it at all. When both the terms of $\beta_D C_D$ and $\beta_H C_H$ are much smaller than unity, Eq. (3) reduces to

$$P = P_{D0}\{1+\beta_D(C_{D_2}+C_{D_1})\} + P_{H0}\{1+\beta_H(C_{H_2}+C_{H_1})\} \quad (6)$$

where

$$P_{D0} = k_D D_{D0} \quad (7)$$

$$P_{H0} = \frac{C_H' b D_{H0}}{(1+bP_1)(1+bP_2)} \quad (8)$$

The permeability data for CO_2 plotted in Figure 4 were fitted to Eq. (3). First, an asymptotic line for the permeability data in the low upstream pressure region at each temperature was assumed as broken line depicted in Figure 4. From the slop and intercept of each broken line, D_{D0} and D_{H0} were determined. The values of such diffusivities at each temperature are listed in Table 3. From the comparison of the permeability data with Eq. (3), β was evaluated by assuming that $\beta_D = \beta_H (= \beta)$. The values of β determined thus are listed in Table 3. The solid curves in Figure 3 represent the calculated results by Eq. (3) with these estimates. β is found to increase with rising temperature.

CONCLUSION

Sorption equilibria for oxygen and carbon dioxide in a homogeneous polycarbonate membrane at different temperatures between 30℃ and 60℃ are described well in terms of the dual-mode sorption model. The conventional dual-mode mobility model has been successfully employed to interpret the observed dependence of the mean permeability coefficient for oxygen on the upstream gas pressure. The pressure dependence of the mean permeability coefficient to carbondioxide is simulated better by a modified dual-mode mobility model with concentration-dependent diffusivities, as encountered in the pressure dependence for the same gas in polystyrene membrane.

NOMENCLATURE

b : Langmuir affinity constant [Pa^{-1}]
C : total sorbed concentration [m^3 (STP)/m^3]
C_D : concentration of Henry's law population [m^3 (STP)/m^3]
C_H : concentration of Langmuir population [m^3 (STP)/m^3]
C_H' : Langmuir capacity constant [m^3 (STP)/m^3]
D : diffusion coefficient in membrane [m^2/s]
J_s : steady-state permeation flux [m^3 (STP)/($\mathrm{m}^2 \cdot \mathrm{s}$)]
k_D : Henry's law constant [m^3 (STP)/($\mathrm{m}^3 \cdot \mathrm{Pa}$)]
$\bar{P}$: mean permeability coefficient [m^3 (STP)$\cdot$m/($\mathrm{m}^2 \cdot \mathrm{s} \cdot \mathrm{Pa}$)]
P : pressure of penetrant gas [Pa]
T_g : glass-transition temperature [℃]
β : concentration-dependence parameter appearing in Eqs. (4) and (5) [m^3/m^3 (STP)]
ΔP : difference between upstream and downstream pressures [Pa]
δ : thickness of membrane [m]

Subscripts

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

REFERENCES

1. Zhou, S. and Stern, S. A.: *J. Polym. Sci.: Part B: Polym. Phys.*, **27**, 205 (1989).
2. Sada, E., Kumazawa, H. and Wang, J. S.: *J. Polym. Sci.: Part B: Polym. Phys.*, **30**, 105 (1992).
3. Bae, S. Y., Cho, D. H., Ko, S. W., Kim, H. T. and Kumazawa, H.: *KJChE.*, **10**, 44 (1993).
4. Sada, E., Kumazawa, H., Xu, P. and Nishigaki, M.: *J. Membrane Sci.*, **37**, 165 (1988).
5. Marquardt, D. W.: *J. Soc. Industr. Math.*, **11**, 2 (1963).