

Sorption and Diffusion of Carbon Dioxide in Polystyrene Membrane

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폴리스티렌 막에서 CO₂의 수착과 확산

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Abstract: The sorption equilibria and permeabilities for CO₂ in a homogeneous membrane of polystyrene with the glass transition temperature of 95°C were measured at a temperature of 60°C and gas pressures up to 1.6 MPa and 2.5 MPa, respectively. The sorption isotherm had the form of dual-mode sorption model at low gas pressures, but became linear at pressures above 1.3 MPa. The linear portion of the isotherm extrapolated to the origin. The pressure dependence of the mean permeability coefficient deviated upward from the dual-mode mobility model prediction. It was found that the glass transition was brought out by the plasticization action of sorbed CO₂ at a gas pressure of 1.3 MPa from the sorption isotherm. And this result was consistent with an increase in the mean permeability coefficient with applied gas pressure.

요 약 : 유리전이온도가 95°C인 폴리스티렌 균질막에서 CO₂의 수착과 투과실험을 온도는 60°C, 수착실험은 1.6 MPa 범위, 투과실험은 2.5 MPa 범위 내에서 각각 행하였다. 낮은 기체압력하에서는 수착등온선이 dual-mode sorption model에 일치하였으나 1.3 MPa 이상에서는 직선이었고, 직선부분은 원점까지 외삽되었다. 평균투과계수의 압력의존성은 dual-mode mobility model로부터 위로 편기되었다. 수착등온선으로부터 폴리스티렌 막은 1.3 MPa의 기체압력에서 수착된 CO₂의 가소 화거동에 의해서 유리전이가 일어난다는 것을 알았고, 이는 평균투과계수의 증가와 일치하였다.

1. Introduction

In our previous work[1], the sorption and permeation behavior for O₂ in polystyrene membrane were investigated in the temperature range of 30°C~50°C. The sorption equilibria for both gases could be described well in terms of a so-called dual-mode

sorption model. The pressure dependence of the mean permeability coefficient for O₂ was simulated by using a dual-mode mobility model, whereas that for CO₂ deviated upward from the dual-mode model prediction specifically in the high pressure region. It was simulated better in terms of a modified dual-mode mobility model proposed by Zhou and Stern

[2]. The upward deviation from the conventional dual-mode model prediction considered to result from the plasticization action of the sorbed CO_2 in the membrane. The plasticization effect here occurred in the diffusion process rather than in the sorption process. This case has been met in the systems of CO_2 -cellulose triacetate and CO_2 -methyl-methacrylate-*n*-butyl copolymer[3] and CO_2 -polystyrene[1].

Concerning the deviation from a dual-mode sorption model, an extended dual-mode model has been proposed by Kamiya et al.[4], in which both Henry's and Langmuir capacity constants were not assumed to be independent of the sorbed amount, but were dependent on the concentration of the sorbed species having the plasticization ability to the polymer. It was shown clearly in the sorption isotherms for several systems of CO_2 -glassy polymer that the plasticization of the polymer induced by a sorbed gas decreased of the excess free volume in the glassy state[4~6].

However, there are no experimental results for the plasticization effect of a sorbed gas on both sorption and permeation processes simultaneously in a moderate pressure range.

In this paper, the sorption equilibria and permeabilities for CO_2 in a polystyrene membrane were measured at 60°C and pressures up to 1.6 MPa and 2.5 MPa, respectively. The plasticization effect of sorbed CO_2 on both the sorption and permeation processes simultaneously exerted in the pressure range covered here.

2. Experimental

Sorption equilibria and permeabilities for CO_2 in a homogeneous membrane of polystyrene (PS) whose glass transition temperature was reported to be 95°C , were measured at 60°C and gas pressures up to 1.6 MPa and 2.5 MPa, respectively. The apparatus and procedures for equilibrium sorption and permeation experiments can be referred to ref[1].

3. Results and Discussion

The upper figure of Fig. 1 shows the sorption isotherm of CO_2 in PS membrane at 60°C . At 30°C to 50°C , the sorption isotherm of CO_2 in PS satisfactorily obeyed a so-called dual-mode sorption model[1].

$$C = C_0 + C_{H_1} = k_D P + \frac{b C_H' P}{1 + b P} \quad (1)$$

whereas at 60°C , the isotherm has the form of the dual-mode model only in the low pressure region and becomes linear at gas pressures above 1.3 MPa as rubbery polymers do. The glass transition temperature(T_g) of PS in the absence of sorbed CO_2 has been reported to be 95°C , but here the sorption of CO_2 might result in a depression of T_g continuously as the amount of CO_2 sorbed increases. This figure illustrates that the glass transition temperature for the polymer- CO_2 mixture approaches the sorption temperature of 60°C when 1.3 MPa of CO_2 pressure is maintained at equilibrium. The isotherm at pressures above 1.3 MPa becomes linear and ex-

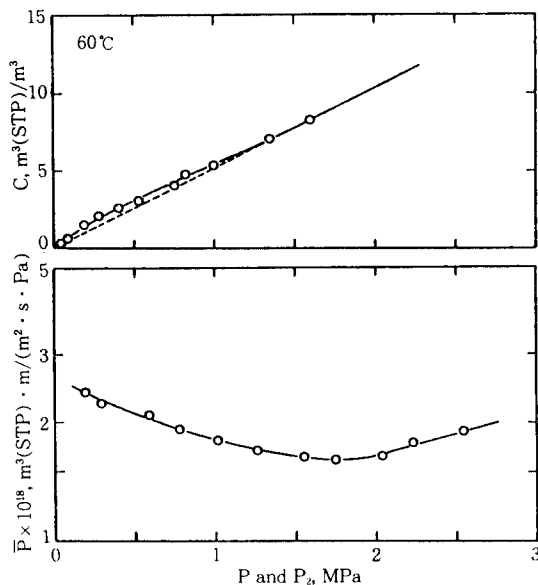


Fig. 1. Sorption isotherm and pressure dependence of mean permeability coefficient for CO_2 in PS membrane at 60°C .

trapolates to the origin. This trend can be understood if the polymer is in its rubbery state. The value of Henry's law constant (k_D) at 60°C along with those at 30°C~50°C[1] are shown as van't Hoff plot in Fig. 2. The Henry's law constant is shown to decrease continuously with increasing temperature in this temperature range.

For the system of PS-CO₂ at 60°C, the plasticization effect of sorbed CO₂ on the polymer might result in a decrease of the unrelaxed microvoid in the glassy state and in a depression of T_g . In other words, the glass transition is brought out by the sorbed CO₂ at temperatures below T_g of the pure polymer. According to an extended dual-mode sorption model proposed by Kamiya et al.[4], the Langmuir capacity constant (C_H') has been given as,

$$C_H' = C_{H0}' (1 = C^*/C_g) \quad (2)$$

where C_{H0}' is the Langmuir capacity constant in the limit of zero gas pressure, C_g the glass transition

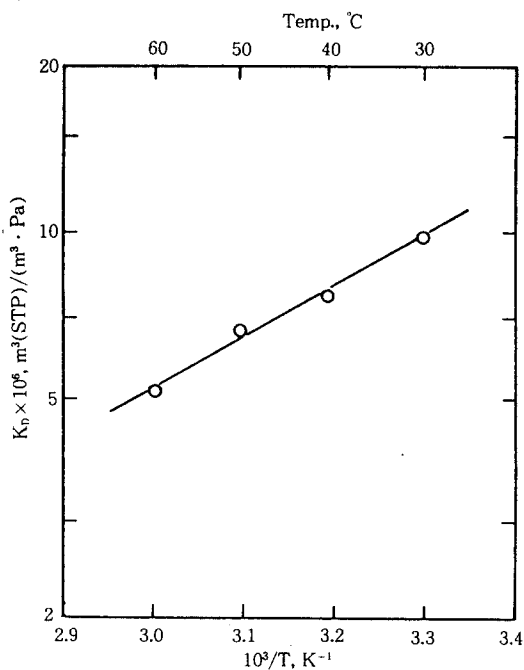


Fig. 2. Temperature dependence of Henry's law constant for CO₂ in PS membrane.

concentration, and C^* the effective concentration for plasticization by a sorbed gas. In the limit of $C^* \rightarrow C_g$, the concentration of Langmuir species is equal to zero, and this is consistent with the present experimental observation.

The lower figure of Figure 1 demonstrates the pressure dependence of the mean permeability coefficient to CO₂ at 60°C. The mean permeability coefficients to the same gas at 30°C~50°C have been found to decrease with increasing upstream gas pressure[1], which could be interpreted in terms of a modified dual-mode mobility model[1] proposed by Zhou and Stern[2] rather than the conventional dual-mode mobility model. The modified model postulates that all of dual-mode sorption parameters are constant but the diffusivities of Henry's law and Langmuir species should depend on the concentration of the respective species:

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

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

The mean permeability coefficient expression can be analytically derived as

$$\bar{P} = \frac{D_{D0}}{\beta_D (P_2 - P_1)} [\exp(\beta_D C_{D2}) - \exp(\beta_D C_{D1})] + \frac{D_{H0}}{\beta_H (P_2 - P_1)} [\exp(\beta_H C_{H2}) - \exp(\beta_H C_{H1})] \quad (5)$$

In the limit of $\beta_D \rightarrow 0$ and $\beta_H \rightarrow 0$, equation (5) reduces to

$$\bar{P} = k_D D_D + \frac{b C_H' D_H}{(1 + b P_1)(1 + b P_2)} \quad (6)$$

which conforms to the permeability expression in terms of so-called dual-mode mobility model[7].

The pressure dependence of the permeability at 60°C is similar at pressures below about 1.6 MPa with the result published in the literature at the temperature of 30°C~50°C[1]. Whereas at pressures above 2.0 MPa, the logarithm of the permeability increases in the logarithm of the permeability with upstream pressure could be caused by the plasticization action by sorbed CO₂ in a rubbery polymer. The linear increase of the sorption isotherm at pressures

above 1.3 MPa which is one of the characteristics of the rubbery polymers might be considered to result from the plasticization action of the sorbed CO₂ in the polymer. The plasticization action to the rubbery polymer here occurs in the diffusion process rather than in the sorption process at gas pressures below 2.5 MPa. The plasticization action in the glassy state of polymer, however, might decrease the unrelaxed microvoids both in the sorption process and in the diffusion process.

4. Conclusion

The sorption isotherm and the pressure dependence of the mean permeability coefficient for CO₂ in polystyrene membrane at 60°C did not obey the conventional dual-mode model. The sorption isotherm has the form of dual-mode sorption model only at low pressures, but obeys a linear relationship passing through the origin at pressure above 1.3 MPa. The pressure dependence of the mean permeability coefficient deviated upward from the dual-mode mobility model prediction. In this system, the glass transition might be brought out by sorbed CO₂ at a gas pressure of 1.3 MPa, consistent with an increase in the permeability with applied gas pressure.

Nomenclature

b	Langmuir affinity constant, Pa ⁻¹
C	total sorbed concentration, m ³ (STP)/m ³
C_D	concentration of Henry's law dissolution species, m ³ (STP)/m ³
C_r	glass transition concentration in eq. (2), m ³ (STP)/m ³
C_H	concentration of Langmuir adsorption species, m ³ (STP)/m ³
C_H'	Langmuir capacity constant, m ³ (STP)/m ³
C^*	effective concentration for plasticization by sorbed gas, m ³ (STP)/m ³

D	diffusion coefficient in membrane, m ² /s
k_D	Henry's law constant, m ³ (STP)/(m ³ Pa)
\bar{P}	mean permeability coefficient or permability, m ³ (STP)m/(m ² s Pa)
P	pressure of penetrant gas or sorbate gas, Pa or MPa
T	temperature, K
T_g	glass transition temperature, °C
β	concentration-dependent parameter in eq.(3) and (4), m ³ /m ³ (STP)

Subscripts

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

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