

Sorption and Permeation Behavior for CO₂ in NH₃-Plasma-Treated and Untreated Polystyrene Membranes

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ABSTRACT: In our preceding work, the simultaneous deviation from the conventional dual-mode sorption and mobility model was observed in a case of CO₂ in polystyrene (PS) membrane (glass transition temperature of pure polymer = 95°C) at 60 and 70°C. The plasticization effect of sorbed CO₂ on both the sorption and diffusion processes tends to be brought about in glassy polymer membranes near the glass transition temperature. The behavior was simulated based on the concept that only one population of sorbed gas molecules of plasticizing ability to the polymer should exist. In the present work, the sorption and permeation behavior for CO₂ in NH₃-plasma-treated and untreated PS membranes at 40°C was investigated, where NH₃-plasma treatment was executed at plasma discharge powers of 40, 80, 120, and 160 W for an exposure time of 2 min. The sorption isotherm could be described by the sorption theory of Mi et al. (Macromolecules 1991, 24, 2361), where the glass transition temperature is depressed by a concentration of

sorbed CO₂ of plasticizing ability. NH₃-plasma treatment on PS membrane had little influence on the sorption behavior of CO₂ at plasma discharge powers up to 160 W. The mean permeability coefficients were somewhat increased only at a discharge power of 160 W. At CO₂ pressures below 0.9 MPa, the pressure dependencies of mean permeability coefficients for CO₂ in both NH₃-plasma-treated and untreated PS membranes at 40°C could also be simulated on the basis of the concept that only one population of sorbed gas molecules of plasticizing ability should exist. At CO₂ pressures above 0.9 MPa, however, a plasticization action of sorbed CO₂ had much more influence on the diffusion process rather than on the sorption one, and such a combined concept underestimated the mean permeability coefficient. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1798–1805, 2007

Key words: diffusion; gas sorption; gas permeation; plasma treatment; polystyrene

INTRODUCTION

The dual-mode sorption and mobility model has been widely applied to simulate sorption and diffusion behavior of a gas in the glassy polymer membrane. The dual-mode sorption model postulates that the sorbed gas molecule in a polymer is present as two species: a Henry's law species, which is dissolved in the polymer matrix, and a Langmuir species, which is adsorbed or filled in unrelaxed microvoids of the polymer. The dual-mode mobility model presumes that these two species execute diffusive movements with different mobilities while being at local equilibrium with each other.

In the original dual-mode sorption model, all of sorption parameters are assumed to be constant irrespective of the concentration of sorbed species. Recently, an extended dual-mode sorption model has been proposed by Kamiya et al.¹ that both Henry's

law constant and Langmuir capacity constant are influenced by the concentration of sorbed species of the plasticizing ability to the polymer.

Similarly, in the original dual-mode mobility model, the diffusivities of both Henry's law and Langmuir species are also assumed to be constant. Concerning this premise, a modified dual-mode mobility model has been proposed by Zhou and Stern² that the diffusivities of both species depend on the concentration of the respective species, because sorbed gas molecules tend to plasticize the polymer membrane. But, in turn, the dual-mode sorption parameters here are assumed not to be affected by the concentration of sorbed gas molecules.

To take the plasticization effect of sorbed gas molecules on both the sorption and diffusion processes into account, a modified dual-mode mobility model² should be considered along with an extended dual-mode sorption model¹ on the basis of the dual-mode concept. But, too many (i.e., nine) parameters are involved in such a combined model, and it is unrealistic for the sake of comparison with the experimental results. It is hoped to develop a more simple model describing the simultaneous deviation from the dual-mode model.

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Mi et al. derived a new relation to express the sorption isotherm of plasticizing penetrants, which is based on a theoretical consideration and has only one parameter.³ Their sorption isotherm can simulate an inflection point at high penetrant pressures as the extended dual-mode sorption model¹ does. The sorption theory of Mi et al.³ tacitly based on the concept that only one population of sorbed molecules exists. Accordingly, the diffusion (mobility) model that is combined with the sorption theory of Mi et al.³ should have the same concept stated earlier.

In our preceding work,^{4,5} a gas-polymer-matrix model proposed by Raucher and Sefcik⁶ was combined with the sorption theory of Mi et al.³ because of the same concept that one population of sorbed molecules exists. The sorption and diffusion behavior influenced by the plasticization action of sorbed gas molecules was described by such a combined model. The sorption equilibria and the pressure dependencies of the mean permeability coefficients for CO₂ in poly(4-methyl-1-pentene), polystyrene, and cellulose triacetate membranes were interpreted satisfactorily by the combined model. The sorption and permeation behavior in glassy polymer membrane at temperatures considerably below the glass transition temperature of pure polymer must basically be simulated by the same combined model as well.

In the present work, first the sorption equilibrium and the pressure dependency of mean permeability coefficient at 40°C for CO₂ in NH₃-plasma-treated and untreated polystyrene (PS) membranes, whose glass transition temperature of pure polymer was reported to be 95°C, were compared with the predictions by the combined model. Second, the effects of NH₃-plasma treatment on the sorption and permeation behavior for CO₂ were investigated.

THEORETICAL BACKGROUND

Dual-mode sorption and mobility model

The dual-mode sorption model postulates that the sorbed gas in a glassy polymer is present as two species: a Henry's law species, which is dissolved in the polymer matrix, and a Langmuir species, which is adsorbed in unrelaxed microvoids of the polymer. The sorption isotherm can be described by the mathematical relationship

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

The two sorbed species, which are termed Henry's law and Langmuir species, respectively, can execute diffusive movements with different mobilities while being at local equilibrium with each other. This parallel approach has been called dual-mode mobility model. The permeation flux in terms of the propor-

tionality to the concentration gradient can be described as

$$J = -D_D(dC_D/dx) - D_H(dC_H/dx) \quad (2)$$

After integrating Eq. (2) over p from p_2 to p_1 with J constant under the steady-state (J_s) assuming sorption and diffusion parameter constant, one gets the mean permeability coefficient (P) defined by

$$P = J_s \delta / (p_2 - p_1) \quad (3)$$

as follows:

$$P = k_D D_D + C'_H b D_H / \{(1 + b p_1)(1 + b p_2)\} \quad (4)$$

In this model, all of the dual-mode sorption and mobility parameters are assumed to be constant irrespective of the sorbed amount.

Deviation from dual-mode sorption and mobility model

To describe the deviation from the original dual-mode sorption model, an extended dual-mode sorption model was proposed by Kamiya et al.,¹ that both Henry's law constant and Langmuir capacity constant are influenced by the concentration of sorbed species of the plasticizing ability to the polymer. They showed clearly in the sorption isotherms in several systems of CO₂-glassy polymer that the plasticization to the polymer caused by sorbed gas resulted in a decrease in the excess free volume in the glassy state and brought about the glass transition at temperatures below nominal glass transition points of the pure polymer.

According to the extended dual-mode sorption model,¹ the concentration of sorbed gas is written as

$$C = C_D + C_H = [k_D \exp(\sigma C^*)] p + C'_{H0} b p (1 - C^*/C_g) / (1 + b p) \quad (5)$$

That is, the concentrations of dissolved (Henry's law) and adsorbed (Langmuir) species are given by

$$C_D = [k_D \exp(\sigma C^*)] p \quad (6)$$

$$C_H = C'_{H0} b p (1 - C^*/C_g) / (1 + b p) \quad (7)$$

In the above equations, C'_{H0} and C_g refer to the Langmuir capacity constant at the limit of $p \rightarrow 0$ and the glass transition concentration, respectively, and σ is the parameter characterizing the concentration dependence of C_D/pC^* denotes the effective concentration for plasticization by sorbed gas defined as

$$C^* = C_D + f C_H \quad (8)$$

where f is the ratio of the plasticizing ability of Langmuir species to that of Henry's law species. When C^* approaches C_g , the concentration of Langmuir species becomes equal to zero according to Eq. (7). That is, the glass transition is brought about by the sorbed gas at temperatures below the glass transition point of the pure polymer. Thus, C_g is termed glass transition concentration.

Zhou and Stern modified the dual-mode mobility model to polymer-gas system in which sorbed gas molecules plasticize the polymer.² In their model, the diffusivities of dissolved and adsorbed species depend on the concentration of corresponding species,

$$D_D = D_{D0} \exp(\beta_D C_D) \quad (9)$$

$$D_H = D_{H0} \exp(\beta_H C_H) \quad (10)$$

while the dual-mode sorption parameters are not affected by the concentration of sorbed species.

With diffusivities for dissolved and adsorbed species in eqs. (9) and (10), the diffusion flux can be expressed as

$$J = -D_{D0} \exp(\beta_D C_D) (dC_D/dx) - D_{H0} \exp(\beta_H C_H) (dC_H/dx) \quad (11)$$

with J constant at steady-state (J_s), the integration from the upstream side to the downstream side of the membrane yields⁷

$$J_s \delta = (D_{D0}/\beta_D) [\exp(\beta_D C_{D2}) - \exp(\beta_D C_{D1})] + (D_{H0}/\beta_H) [\exp(\beta_H C_{H2}) - \exp(\beta_H C_{H1})] \quad (12)$$

The mean permeability coefficient is derived as⁷

$$P = [D_{D0}/\{\beta_D(p_2 - p_1)\}] [\exp(\beta_D C_{D2}) - \exp(\beta_D C_{D1})] + [D_{H0}/\{\beta_H(p_2 - p_1)\}] [\exp(\beta_H C_{H2}) - \exp(\beta_H C_{H1})] \quad (13)$$

The value of P calculated by Eq. (14) is in complete agreement with that numerically calculated by Zhou and Stern.²

To take the plasticization effect of sorbed gas molecules on both the sorption and diffusion processes into account, the modified dual-mode mobility model³ should be combined with the extended dual-mode sorption model.¹

In reality, Eq. (13) based on a modified dual-mode mobility model (i.e., combination of conventional dual-mode sorption model and modified dual-mode mobility model) has the same form as that based on a modified dual-mode model (i.e., combination of extended dual-mode sorption model and modified dual-mode mobility model), but it should be noted that C_{D2} and C_{H2} in the dual-mode model must be

determined by a trial and error procedure from Eq. (6) to (8), according to an extended dual-mode sorption model. This combined model is regarded as one of the most elaborated models for gas permeation in glassy polymer membranes. But, too many parameters (nine; five sorption parameters, k_D , σ , b , C'_{H0} , f , and four diffusion parameters, D_{D0} , D_{H0} , β_D , β_H) to be adjusted are contained in such a combined model. It is unrealistic for the sake of comparison with the experimental results.

Single-mode sorption and mobility model for a glassy polymer membrane

Mi et al. proposed the following equation for the concentration of a plasticizing penetrant dissolved in a glassy polymer at pressure p and temperature T .³

$$C = S_0 p \exp\{A[T_g(C)(T_g(C) - T_g(0)) / (T_g(0) - T) / (T_g(0))^2]\} \quad (14)$$

where S_0 is a solubility coefficient at the limit of $p \rightarrow 0$, and $T_g(0)$ and $T_g(C)$ are the glass transition temperatures of the polymer containing a dissolved penetrant at concentration of 0 (i.e., pure polymer) and C , respectively. It should be noted that Eq. (14) contains only one adjustable parameter A , though it is an implicit equation for C . For S_0 can be measured, $T_g(0)$ is generally known or can be measured, and $T_g(C)$ can be estimated from the relation of Chow.⁸

Equation (14) tacitly is based on the assumption that only one population of sorbed gas molecules exists as a gas-polymer-matrix model proposed by Raucher and Sefcik⁶ does. According to the gas-polymer-matrix model, the diffusivity for a penetrant gas in polymer can be written as

$$D = D_0 \exp(\beta C) \quad (15)$$

where β is a parameter describing the magnitude of gas-polymer interactions and D_0 refers to the diffusivity at the limit of $p \rightarrow 0$. Hence, Eq. (15) also has only one adjustable parameter (β). The permeation flux (J) can be written as

$$J = -D_0 \exp(\beta C) dC/dx \quad (16)$$

Similarly, with J constant at a steady-state (J_s), the integration from the upstream side to the downstream side of the membrane gives the permeability coefficient (P):

$$P = J_s \delta / (p_2 - p_1) = D_0 [\exp(\beta C_2) - \exp(\beta C_1)] / [\beta (p_2 - p_1)] \quad (17)$$

If Eq. (17) is combined with Eq. (14), only two parameters (A and β) to be adjusted are contained.

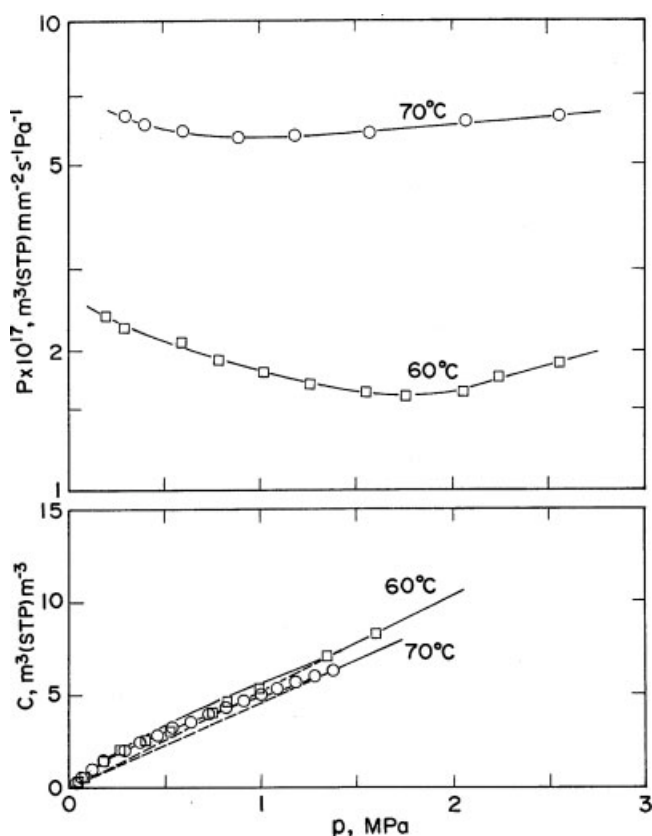


Figure 1 Sorption isotherms and pressure dependencies of mean permeability coefficients for CO₂ in PS membrane at 60 and 70°C.

Recently, a nonlinear model for non-Fickian diffusion in polymer-penetrant systems was proposed by introducing concentration dependencies in the transport parameters.^{9,10} The diffusion flux in terms of this nonlinear model is composed of diffusion flux based on Fick's law and non-Fickian effects due to the coupling to molecular relaxation. Actually, the model contains six dimensionless parameters; four characterize the polymer-penetrant system while the other two do the driving force for sorption. It should be noted that the model predicted a number of observable trends.¹⁰ Especially, the model predictions were compared successfully with sorption data of acetone in a glassy random copolymer of *p*-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid.¹¹ Whereas, the diffusion flux described by either Eq. (11) or (16) is based on just Fick's law.

EXPERIMENTAL

Homogeneous polystyrene (PS) membrane samples were kindly supplied from Mitsubishi-Monsanto Chemical, Japan. The glass transition temperature of pure polymer was reported to be 95°C by the manufacturer. The plasma treatment was conducted using a plasma reactor (PLASMA SYSTEM 440, Tepla). NH₃

was used as the treatment gas, and the flow rate was maintained at 30 cm³ (STP)/min. The glow discharge was generated under a pressure of 0.05 Torr at a fixed frequency of 2.45 GHz. The input power of discharge was varied up to 160 W. The exposure time was fixed at 2 min.

Sorption equilibria for CO₂ were measured at 40°C by a pressure decay method, where the pressure in the sorption cell was continuously measured by means of pressure transducer. The steady-state permeation rates for CO₂ were measured at the same temperature by a valuable-volume method. The gas (CO₂) to be permeated was fed into the upstream side, while the downstream side was filled with the same gas at an atmospheric pressure. The volumetric flow rate through the membrane to the downstream side was measured by observing the displacement of a small amount of 1-propanol in a capillary tube connected to the downstream side. The permeability coefficient was calculated from this steady-state permeation flux. The permeation area of the cell was 19.6 cm².

DISCUSSION

Sorption and permeation behavior of PS membrane at 60 and 70°C⁴

The sorption isotherms for CO₂ in PS membranes at 60 and 70°C, in our preceding paper,⁴ are shown in the lower panel of Figure 1. At each temperature, the isotherm has the form of the dual-mode model only in the low pressure region and becomes linear at gas pressure above 1.4 or 1.2 MPa. The glass transition temperature (T_g) of PS in the absence of sorbed CO₂ has been reported to be 95°C ($= T_g(0)$), but here sorption of CO₂ might result in a depression of T_g continuously with increasing amount of sorbed CO₂. This figure implies that the glass transition temperature for the polymer-CO₂ mixture approaches the sorption temperature, 60 and 70°C when equilibrated with 1.4

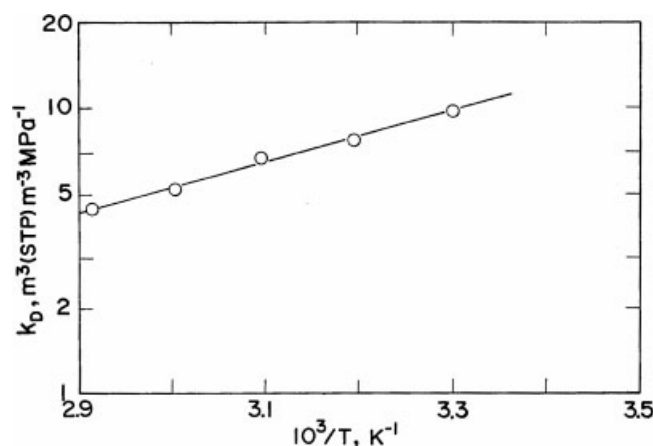


Figure 2 Temperature dependence of Henry's law constants for CO₂ in PS membrane.

TABLE I
Values of Parameters A and S_0 Involved in Eq. (14) for CO_2 in PS Membrane

Membrane	Temp. (°C)	A (K^{-1})	S_0 [$\text{m}^3(\text{STP})\text{m}^{-3}\text{MPa}^{-1}$]	k_D [$\text{m}^3(\text{STP})\text{m}^{-3}\text{MPa}^{-1}$]
PS	40	0.09	14.3	7.6
PS	60	0.17	8.59	5.2
PS	70	0.37	8.19	4.5

and 1.2 MPa of CO_2 pressure, respectively. The isotherm at pressures above 1.4 or 1.2 MPa exhibits a straight line passing through the origin, since the polymer is in a rubbery state. From the slope of the straight line, the value of Henry's law constant (k_D) can be calculated by

$$C = k_D p \quad (18)$$

The values of Henry's law constant calculated from the slopes of the linear portions of the isotherms at 60 and 70°C are plotted in Figure 2, together with those at 30–50°C taken from our preceding papers.^{4,12} The Henry's law constant is shown to continuously decrease with rising temperature on the van't Hoff plot in the temperature range of 30–70°C.

The full curves at 60 and 70°C in the lower panel of Figure 1 represent the calculated ones by Eq. (14) proposed by Mi et al.,³ wherein $T_g(C)$ is replaced by

$$T_g(C) = T_g(0) - \alpha_c C \quad (19)$$

The values of a and S_0 involved in Eq. (14) are listed in Table I.

The upper panel of Figure 1 indicates the pressure dependence of the mean permeability coefficients to CO_2 at 60 and 70°C.⁴ At 60°C, the pressure dependence of the mean permeability coefficient has the similar form at pressures below ~1.6 MPa to those at temperatures of 30–50°C, whereas at pressures above 2.0 MPa, the logarithm of the permeability increases linearly with upstream gas pressure. The linear increase in the logarithmic permeability with upstream pressure reminds us of the plasticization action by sorbed CO_2 in a rubbery polymer. In view of the experimental evidence that at pressures above 1.4 MPa the sorption isotherm becomes linear, characteristic of rubbery polymers, such a linear increase might be ascribed to the plasticization action of sorbed CO_2 to the rubbery polymer. At 70°C, the logarithm of the mean permeability coefficient increases linearly with upstream gas pressure above 1.2 MPa, which is lower than 60°C (1.6 MPa).

Figure 3 shows the comparison of the observed pressure dependencies of the mean permeability coefficients for CO_2 in PS at 60 and 70°C with the predictions by Eq. (17) combined with Eq. (14). The full curves represent the predictions with the values of the

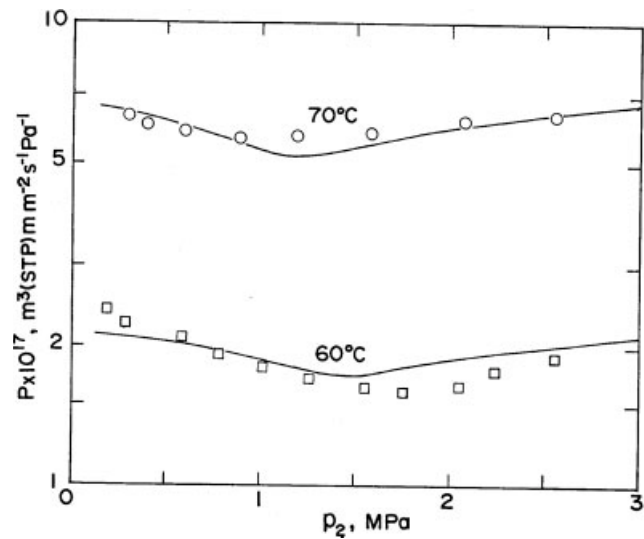


Figure 3 Comparison of mean permeability coefficient for CO_2 in PS membrane at 60 and 70°C with the prediction by the proposed model.

parameters (β and D_0) listed in Table II. It is apparent that Eq. (17) combined with Eq. (14), i.e., a combination of a gas-polymer-matrix model⁶ with the sorption theory of Mi et al.,³ can approximately simulate the permeation behavior.

Sorption and permeation behavior of PS membrane at 40°C

Figure 4 shows the sorption isotherms for CO_2 in NH_3 -plasma-treated and untreated polystyrene (PS) membranes at 40°C. The sorption isotherms of both plasma-treated and untreated PS membranes exhibited downward concave patterns, characteristic of glassy polymers. NH_3 -plasma treatment on PS membrane seems to have little influence on the sorption behavior of CO_2 at plasma discharge powers up to 160 W. Thus, so far, the sorption behavior has been described in terms of the dual-mode sorption model, i.e., Eq. (1). But here the applicability of Eq. (14) will be examined. Equation (14) was successfully applied to the sorption isotherms of CO_2 in PS membrane at 60 and 70°C as depicted in Figure 1. The full curve in

TABLE II
Values of Parameters β and D_0 Involved in Eq. (15) for CO_2 in PS Membrane

Membrane	Temp. (°C)	β [$\text{m}^3 \text{m}^{-3}(\text{STP})$]	$D_0 \times 10^{18}$ [$\text{m}^2 \text{s}^{-1}$]
PS	40	0.025	1.06
PS ^a	40	0.025	1.17
PS	60	0.04	3.01
PS	70	0.05	10.05

^a NH_3 -plasma-treated (160 W, 2 min).

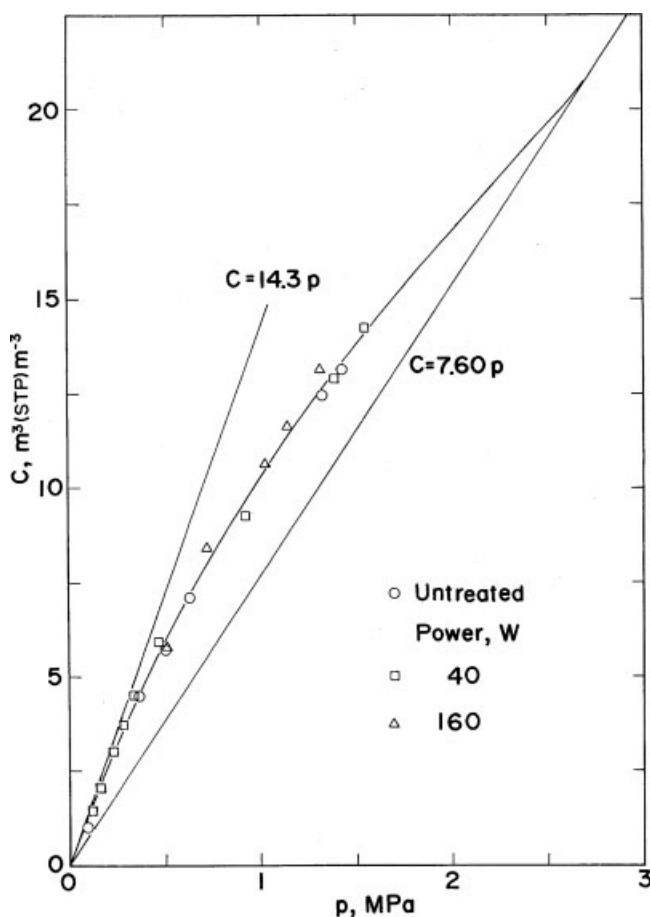


Figure 4 Sorption isotherms for CO₂ in PS membranes with and without NH₃-plasma treatment at 40°C.

Figure 4 represents a sorption isotherm calculated by Eq. (14) with estimates A ($= 0.09 \text{ K}^{-1}$) and S_0 ($= 14.3 \text{ m}^3 \text{ (STP) m}^{-3} \text{ MPa}^{-1}$), which fits to all of the sorption data at 40°C. The values of A and S_0 were listed in Table I, along with those at 60 and 70°C. One of the straight lines represents Eq. (18) with $k_D = 7.60 \text{ m}^3 \text{ (STP) m}^{-3} \text{ MPa}^{-1}$. This k_D value at 40°C was read out in Figure 2. The other straight line represents Eq. (18) at the limit of $p \rightarrow 0$, i.e.,

$$C = S_0 p \quad (20)$$

To calculate $T_g(C)$ in Eq. (5) by Eq. (10), the value of glass transition concentration C_g ($T(C_g) = \text{experimental temperature } 313 \text{ K}$ in this case) is needed. The value of C_g was assumed to be $21.0 \text{ m}^3 \text{ (STP) m}^{-3}$ (whereat $p = 2.76 \text{ MPa}$), and hence the value of α_c was calculated to be 2.62 K^{-1} . Even when the experimental temperature is considerably low as compared to the glass transition temperature of the pure polymer $T_g(0)$, the sorption isotherm of CO₂ can also be described by Eq. (14), i.e., single-mode sorption model incorporating a depression of the glass transition temperature caused by sorbed CO₂ of plasticization ability, instead of dual-mode sorption model.

Figure 5 shows the pressure dependencies of the mean permeability coefficients to CO₂ in PS membranes with treated NH₃-plasma at discharge powers of up to 160 W and an exposure time of 2 min. The mean permeability coefficients of NH₃-plasma-treated membranes at discharge powers of up to 120 W could not be distinguished from those of untreated membranes. Only at a discharge power of 160 W, the mean permeability coefficients were somewhat increased. Figure 5 also indicates the comparison of the observed pressure dependencies of the mean permeability coefficients for the two cases with the predictions by Eq. (17) combined with Eq. (14). The full curves represent the predictions with the values of the parameters (β and D_0) listed in Table II. It is apparent that Eq. (17) combined with Eq. (14), i.e., a combination of a gas-polymer-matrix model⁶ with the sorption theory of Mi et al.³ can approximately simulate the permeation

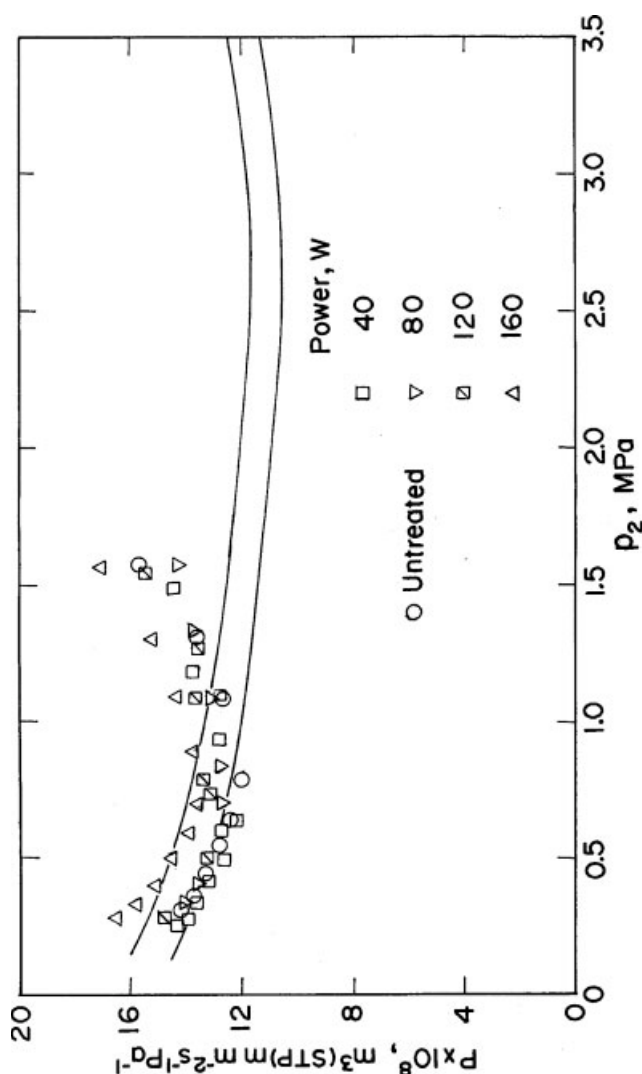


Figure 5 Pressure dependencies of mean permeability coefficients for CO₂ in PS membranes with and without NH₃-plasma treatment at 40°C.

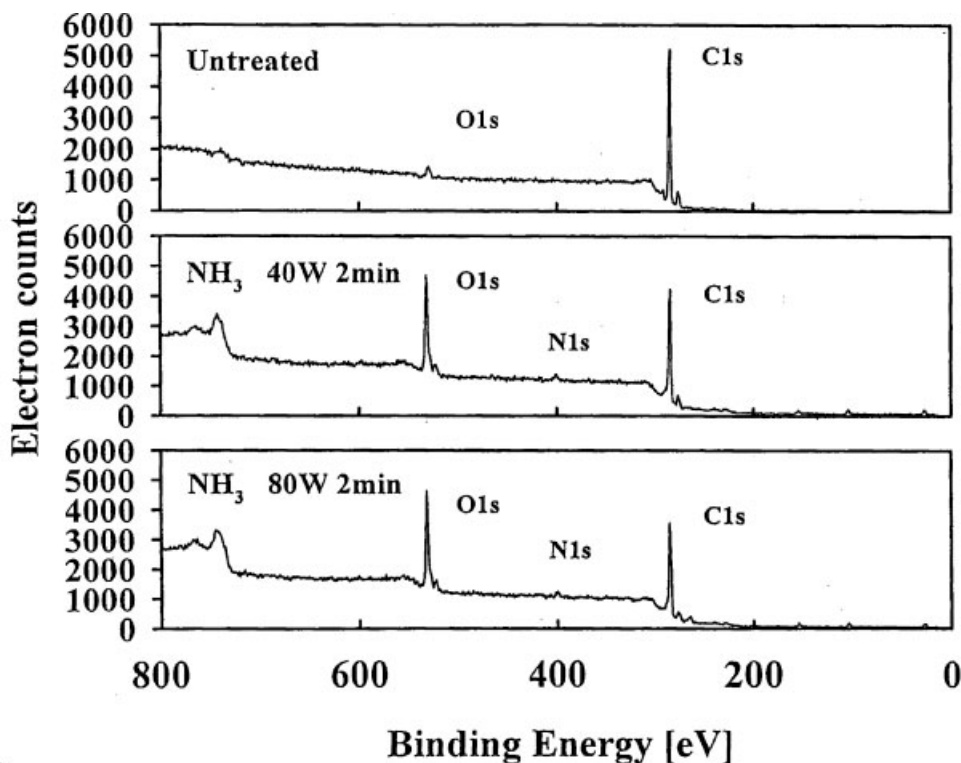


Figure 6 ESCA spectra of PS membranes with and without treated NH_3 -plasma.

behavior for CO_2 pressures below 0.9 MPa. With increasing CO_2 pressure above 0.9 MPa, the observed permeability coefficient increases, while the mean permeability coefficient predicted on the basis of Eq. (17) combined with Eq. (14), keeps on slightly decreasing. At CO_2 pressures above 0.9 MPa, a plasticization action of sorbed CO_2 is believed to exert an influence much more on the diffusion process than on the sorption one, though the sorption isotherm subjected to the plasticization of sorbed CO_2 could be described by the sorption theory of Mi et al.³ The effect of plasticization action of sorbed CO_2 on the diffusion process must essentially be exerted at CO_2 pressures above 2.76 MPa ($C_g = 21.0 \text{ m}^3 \text{ (STP)/m}^{-3}$) as depicted in Figure 4. In fact, the simultaneous deviation from the conventional dual-mode sorption and mobility model had been observed in the case of CO_2 in PS membrane at 60 and 70°C, in which the plasticization effect of sorbed CO_2 on both the sorption and diffusion processes had been brought about in PS membrane near the glass transition temperature. At 40°C, however, the gas-polymer matrix model,⁶ incorporating the sorption theory of Mi et al.,³ tends to underestimate the mean permeability coefficient. Such an underestimation may be caused by non-Fickian effects due to the coupling to molecular relaxation.¹⁰

Figure 6 demonstrates the ESCA spectra of PS membranes with and without treated NH_3 -plasma. Actually, the N1s peak definitely appears in NH_3 -plasma-treated PS membranes, presumably based on

NH_2 group. Certainly, this basic functional group generated by NH_3 -plasma treatment possibly exerts an interaction with dissolved CO_2 to promote the permeation flux. But the height of N1s peak was rather low, so that the mean permeability coefficient to CO_2 was a little bit increased only at a discharge power of 160 W.

CONCLUSIONS

The sorption and permeation behavior for CO_2 in NH_3 -plasma-treated and untreated PS membranes at 40°C was investigated. The sorption isotherm could be described by the sorption theory of Mi et al., where the glass transition temperature is depressed by a concentration of sorbed CO_2 of the plasticizing ability. NH_3 -plasma treatment on PS membrane had little influence on the sorption behavior of CO_2 at plasma discharge powers up to 160 W. The mean permeability coefficients of NH_3 -plasma-treated membranes at discharge powers up to 120 W could not be distinguished from those of untreated membranes. Only at a discharge power of 160 W, the mean permeability coefficients were somewhat increased. At CO_2 pressures below 0.9 MPa, the pressure dependencies of mean permeability coefficients for CO_2 in both NH_3 -plasma-treated and untreated PS membranes at 40°C could be also simulated on the basis of the concept that only one population of sorbed gas molecules should exist. At CO_2 pressures above 0.9 MPa, how-

ever, a plasticization action of sorbed CO₂ had much more influence on the diffusion process than on the sorption one.

NOMENCLATURE

Symbols

A	parameter involved in Eq. (5) (K^{-1})
B	Langmuir affinity constant (Pa^{-1})
C	concentration of total sorbed species [$\text{m}^3(\text{STP})\text{m}^{-3}$]
C_D	concentration of Henry's law species [$\text{m}^3(\text{STP})\text{m}^{-3}$]
C_g	glass transition concentration [$\text{m}^3(\text{STP})\text{m}^{-3}$]
C_H	concentration of Langmuir species [$\text{m}^3(\text{STP})\text{m}^{-3}$]
C_H'	Langmuir capacity constant [$\text{m}^3(\text{STP})\text{m}^{-3}$]
C^*	effective concentration of plasticization by sorbed gas molecule [$\text{m}^3(\text{STP})\text{m}^{-3}$]
D	diffusion coefficient in membrane (m^2s^{-1})
f	ratio of the plasticizing ability of Langmuir species to that of Henry's law species appearing in Eq. (8)
J	permeation flux [$\text{m}^3(\text{STP})\text{m}^{-2}\text{s}^{-1}$]
k_D	Henry's law constant [$\text{m}^3(\text{STP})\text{m}^{-3}\text{Pa}^{-1}$]
P	mean permeability coefficient [$\text{m}^3(\text{STP})\text{m}^{-2}\text{s}^{-1}\text{Pa}^{-1}$]
p	pressure of penetrant gas (Pa)
S_0	solubility coefficient at the limit of $p \rightarrow 0$ [$\text{m}^3(\text{STP})\text{m}^{-3}\text{Pa}^{-1}$]
T	temperature (K)
T_g	glass transition temperature (K)

x	position coordinate in the net flux direction (m)
α_c	coefficient appearing in Eq. (19) [$\text{K m}^3\text{m}^{-3}(\text{STP})$]
δ	thickness of membrane (m)

Subscript

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

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