

Sorption and Permeation Behavior for a Gas in Glassy Polymer Membrane Near the Glass Transition Temperature

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SYNOPSIS

The deviation from the conventional dual-mode sorption and mobility model for a gas in glassy polymer membranes has separately been studied thus far, and to simulate sorption and diffusion behavior, an extended dual-mode sorption model and a modified dual-mode mobility model, respectively, have been proposed independently. However, simultaneous deviation from the conventional dual-mode sorption and mobility model was observed in cases of CO₂ in poly-4-methyl-1-pentene membrane at 20°C and in polystyrene membrane 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 exists. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The dual-mode sorption and mobility model has been widely used to simulate sorption and diffusion behavior for a gas in glassy polymer membranes. The dual-mode sorption model postulates that 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 in unrelaxed microvoids of the polymer. The dual-mode mobility model assumes 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 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 and Langmuir capacity constants are influenced by the concentration of sorbed species of the plasticizing ability to the polymer. Mi et al.² derived a new relation to express the sorption isotherm of

plasticizing penetrants, which is based on a theoretical consideration and has only one parameter. Their sorption isotherm can simulate an inflection point at high penetrant pressures as the extended dual-mode sorption model¹ does.

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 Stern³: 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 are assumed not to be affected by the concentration of sorbed gas molecules.

To take into account the plasticization effect of sorbed gas molecules on both the sorption and diffusion processes, a modified dual-mode mobility model³ should be considered along with an extended dual-mode sorption model¹ on the basis of the dual-mode concept. But too many (nine) parameters are contained 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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In the present work, the sorption and diffusion behavior influenced by the plasticization action of sorbed gas molecules was described by a gas-polymer-matrix model combined with a sorption theory of Mi et al.² The sorption equilibria and the pressure dependencies of the mean permeability coefficients for CO₂ in poly-4-methyl-1-pentene and polystyrene membranes were interpreted satisfactorily by the proposed combined model.

THEORETICAL BACKGROUND

Deviation from a Dual-Mode Sorption Model

The dual-mode sorption model postulates that sorbed gas 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 in unrelaxed microvoids of the polymer. The sorption isotherm can be described by the mathematical relationship

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

In this model, all the dual-mode sorption parameters are assumed to be constant irrespective of the sorbed amount. Recently, an extended dual-mode sorption model was proposed by Kamiya et al.¹; that both Henry's law and Langmuir capacity constants 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

$$C = C_D + C_H = [k_D \exp(\sigma C^*)] p + \frac{C'_{H0} b p (1 - C^*/C_g)}{1 + b p} \quad (2)$$

i.e., the concentrations of dissolved (Henry's law) and adsorbed (Langmuir) species are given by

$$C_D = [k_D \exp(\sigma C^*)] \quad (3)$$

$$C_H = \frac{C'_{H0} b p (1 - C^*/C_g)}{1 + b p} \quad (4)$$

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

$$C^* = C_D + f C_H \quad (5)$$

where f is the ratio of the plasticizing ability of the Langmuir species to that of Henry's law species. When C^* approaches C_g , the concentration of the Langmuir species becomes equal to zero according to eq. (4), i.e., 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 the glass transition concentration.

The sorption and desorption isotherms for CO₂ in polyvinylbenzoate (PVB) membrane at different temperatures were measured by Kamiya et al.⁴ The glass transition temperature of pure PVB was reported to be 50°C. According to their research,⁴ below 45°C, the sorption isotherms are concave to the pressure axis in the low-pressure range, but become linear with increasing gas pressure (i.e., $\sigma = 0$). Furthermore, the isotherms can be extrapolated back to the origin. The isotherms at 55 and 65°C are almost linear over the whole pressure range. Even below 45°C, PVB seems to be in a rubbery state under the high pressure of CO₂, i.e., the transition from the glassy to the rubbery state is brought about by an increase in gas pressure.

Mi et al.² proposed the following equation for the concentration of a plasticizing penetrant dissolved in a glassy polymer at pressure p and temperature T :

$$C = S_0 p \times \exp\left\{A \left\{ \frac{T_g(C)[T_g(C) - T_g(0)][T_g(0) - T]}{(T_g(0))^2} \right\}\right\} \quad (6)$$

where S_0 is a solubility coefficient in 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 0 (pure polymer) and C , respectively. It should be noted that eq. (6) contains only one adjustable parameter A , as S_0 can be mea-

sured, $T_g(0)$ is generally known or can be measured, and $T_g(C)$ can be estimated from the relation of Chow.⁵

Equation (6) tacitly is based on the assumption that only one population of sorbed gas molecules exists, as assumes a gas-polymer-matrix model proposed by Raucher and Sefcik.⁶

Deviation from a Dual-mode Mobility Model

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 the dual-mode mobility model. The permeation flux in terms of the proportionality to the concentration gradient can be described as

$$J = -D_D \frac{dC_D}{dx} - D_H \frac{dC_H}{dx} \quad (7)$$

After integrating eq. (7) over p from p_2 to p_1 with J constant under the steady state (J_s) assuming sorption and diffusion parameters constant, one gets the mean permeability coefficient (\bar{P}) defined by

$$\bar{P} = J_s \delta / (p_2 - p_1) \quad (8)$$

as follows:

$$\bar{P} = k_D D_D + \frac{C'_H b D_H}{(1 + b p_1)(1 + b p_2)} \quad (9)$$

Zhou and Stern modified the dual-mode mobility model to the polymer-gas system in which sorbed gas molecules plasticized the polymer.³ In their model, the diffusivities of dissolved and adsorbed species depend on the concentration of the corresponding species:

$$D_D = D_{D0} \exp(\beta_D C_D) \quad (10)$$

$$D_H = D_{H0} \exp(\beta_H C_H) \quad (11)$$

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

With the diffusivities for dissolved and adsorbed species in eqs. (10) and (11), the diffusion flux can be expressed as

$$J = -D_{D0} \exp(\beta_D C_D) \frac{dC_D}{dx} - D_{H0} \exp(\beta_H C_H) \frac{dC_H}{dx} \quad (12)$$

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

$$J_s \delta = \frac{D_{D0}}{\beta_D} [\exp(\beta_D C_{D2}) - \exp(\beta_D C_{D1})] + \frac{D_{H0}}{\beta_H} [\exp(\beta_H C_{H2}) - \exp(\beta_H C_{H1})] \quad (13)$$

The mean permeability coefficient is derived as⁷

$$\bar{P} = \frac{D_{D0}}{\beta_D (p_2 - p_1)} [\exp(\beta_D C_{D2}) - \exp(\beta_D C_{D1})] + \frac{D_{H0}}{\beta_H (p_2 - p_1)} [\exp(\beta_H C_{H2}) - \exp(\beta_H C_{H1})] \quad (14)$$

The value of \bar{P} calculated by eq. (14) is in complete agreement with that numerically calculated by Zhou and Stern.³

Simultaneous Deviation from Conventional Dual-mode Sorption and Mobility Model

To take account of the plasticization effect of sorbed gas molecules on both the sorption and diffusion processes, the modified dual-mode mobility model³ should be combined with the extended dual-mode sorption model,¹ but too many (nine) parameters to be adjusted are contained in such a combined model. It is unrealistic for the sake of comparison with the experimental results.

Equation (6) tacitly based on the assumption that only one population of sorbed gas molecules exists contains only one adjustable parameter (A). When combined with eq. (6), a gas-polymer-matrix model proposed by Raucher and Sefcik⁶ should be employed because of the same premise that only one population of sorbed molecules exists. According to the gas-polymer-matrix model, the diffusivity for a penetrant gas in a 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 in the limit of $p \rightarrow 0$. So, eq. (15) also has

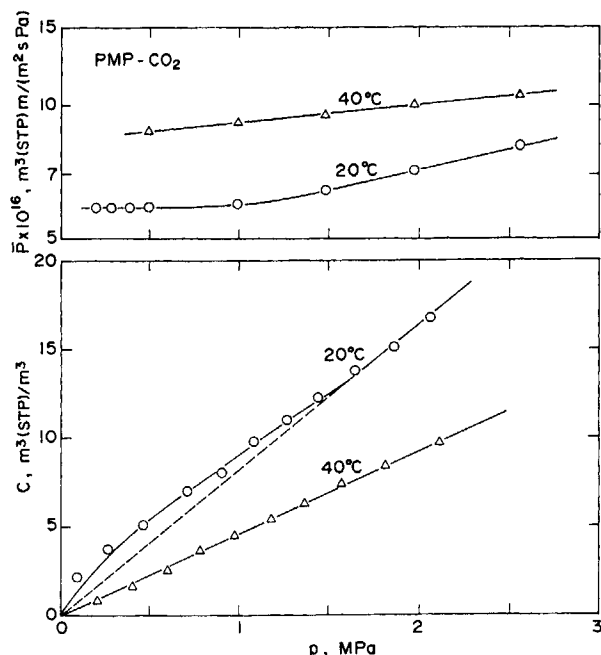


Figure 1 Sorption isotherms and pressure dependencies of mean permeability coefficients for CO₂ in PMP membrane at 20 and 40°C.

only one adjustable parameter (β). The permeation flux can be written as

$$J = -D_0 \exp(\beta C) \frac{dC}{dx} \quad (16)$$

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:

$$\bar{P} = \frac{D_0}{\beta(p_2 - p_1)} [\exp(\beta C_2) - \exp(\beta C_1)] \quad (17)$$

If eq. (17) is combined with eq. (6), only two parameters (A and β) to be adjusted are contained.

EXPERIMENTAL

Though some experimental evidence to the deviation from the dual-mode sorption and mobility model has been available,^{4,7-11} the experiments for sorption and permeation have been newly undertaken. Sorption equilibria and permeabilities for CO₂ in the polystyrene (PS) membrane at 70°C were newly measured to discuss the deviation from the dual-mode model. Homogeneous PS membrane samples were

kindly provided by Mitsubishi-Monsanto Chemical Co., Japan.

Sorption equilibria were determined by the pressure decay method, and gas permeabilities were measured by the variable volume method. A detailed description of procedures for sorption and permeation experiments is found elsewhere.^{8,12}

DISCUSSION

The lower figure of Figure 1 shows the sorption isotherms for CO₂ in the poly-4-methyl-1-pentene (PMP) membrane at 20 and 40°C.³ The isotherm at 40°C is shown to be linear, because PMP is in a rubbery state. At 20°C, the isotherm has the form of a dual-mode sorption model at low gas pressures, but becomes linear (i.e., $\sigma = 0$) like the isotherm at 40°C, at pressures above 1.6 MPa. The glass transition temperature (T_g) in the absence of sorbed CO₂ is ca. 34°C,³ but sorption of CO₂ results in a decrease in T_g continuously as the amount of sorbed CO₂ increases. When equilibrated with ca. 1.6 MPa of CO₂, the T_g for the polymer-CO₂ mixture approaches the sorption temperature, 20°C. The isotherm at pressures above 1.6 MPa becomes linear and extrapolated to the origin since the polymer is in a rubbery state. From the slope of the straight line, the values of Henry's law constant (k_D) can be calculated by

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

and along with that at 30°C⁸ were plotted as a van't Hoff plot in Figure 2. The Henry's law constant is shown to continuously decrease with increasing temperature in the range of 20–40°C, encompassing the glass transition temperature. The full curve at 20°C in the lower figure of Figure 1 represents the

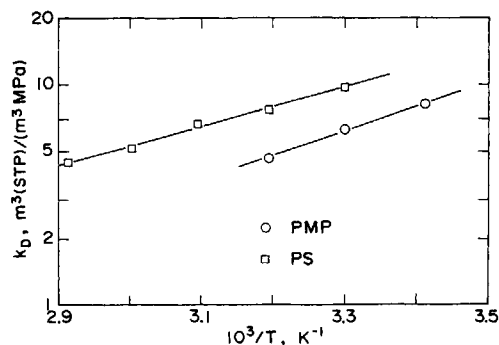


Figure 2 Temperature dependencies of Henry's law constants for CO₂ in PMP and PS membranes.

Table I Values of Parameter A and S_0 Involved in Eq. (6) for CO_2 in PMP and PS Membranes

Membrane	Temp (°C)	A (K^{-1})	$S_0 \times 10^{-6}$ [m^3 (STP)/ m^3 Pa]
PMP	20	0.85	13.6
PS	60	0.17	8.59
PS	70	0.37	8.19

calculated results by eq. (6) proposed by Mi et al.,² wherein $T_g(C)$ is replaced by

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

The values of only A and S_0 are used for drawing the full curve and are listed in Table I.

The upper figure of Figure 1 shows the pressure dependence of the mean permeability coefficient of the PMP membrane to CO_2 at 20 and 40°C, encompassing the glass transition temperature of pure PMP.⁸ The mean permeability coefficients increase with upstream gas pressure. At 40°C, the logarithm of the mean permeability coefficient increases linearly with the upstream gas pressure. At 20°C, the mean permeability coefficient in the low-pressure region remains constant. The experimental evidence that the logarithm of the mean permeability coefficient to CO_2 at 40°C increases with upstream gas pressure can be interpreted by the plasticization action of sorbed CO_2 in a rubbery polymer membrane. At 20°C, the logarithm of the coefficient in the high-pressure region is shown to increase linearly with pressure, and the membrane may change to a rubbery state in the high CO_2 pressure region. The lower figure shows that the inflection in the isotherm at 20°C occurs at 1.6 MPa of CO_2 pressure, and at pressures above 1.6 MPa, the isotherm becomes linear, characteristic of rubbery polymers. The plasticization action to the rubbery polymer tends to emerge in the diffusion process rather than in the sorption process with in the gas pressures covered here (below 2.5 MPa).

The lower figure of Figure 3 shows the sorption isotherms for CO_2 in PS at 60°C taken from our preceding article¹¹ and at 70°C newly measured here. At each temperature, the isotherm has the form of the dual-mode model only in the low-pressure region and becomes linear (i.e., $\sigma = 0$) at gas pressures above 1.4 or 1.2 MPa. The glass transition temperature (T_g) of PS in the absence of sorbed CO_2 has been reported to be 95°C, but, here, sorption of CO_2 might result in a depression of T_g continuously as the amount of sorbed CO_2 increases. This figure im-

plies that the glass transition temperature for the polymer- CO_2 mixture approaches the sorption temperature, 60 and 70°C, when equilibrated with ca. 1.4 and 1.2 MPa of CO_2 , respectively.

Similarly, the full curves in the lower figure of Figure 3 represent the calculated results by eq. (6), wherein $T_g(C)$ is set equal to eq. (19). The values of A and S_0 involved in eq. (6) are also listed in Table I. The values of Henry's law constant calculated from the slopes of the linear portions of the isotherms at 60 and 70°C on the basis of eq. (18) are plotted in Figure 2, together with those at 30–50°C.¹⁰ The Henry's law constant is shown to continuously depress with temperature on the van't Hoff plot in the temperature range of 30–70°C.

The upper figure of Figure 3 indicates the pressure dependence of the mean permeability coefficients to CO_2 at 60°C taken from our preceding article¹¹ and at 70°C measured here. The mean permeability coefficients at 30–50°C have been found to decrease with increasing upstream gas pressure, which can be interpreted in terms of a modified dual-mode mobility model.³ At 60°C, the pressure dependence of the mean permeability coefficient has a form similar at

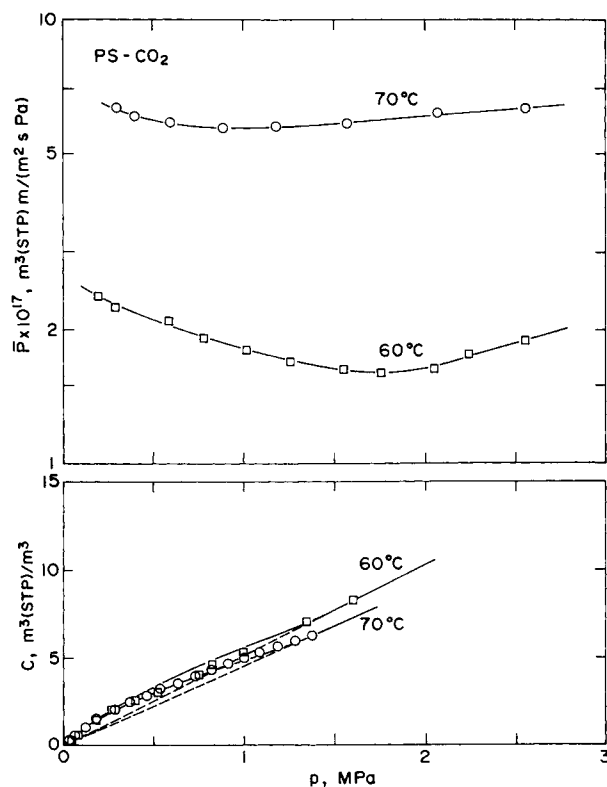


Figure 3 Sorption isotherms and pressure dependencies of mean permeability coefficients for CO_2 in PS membrane at 60 and 70°C.

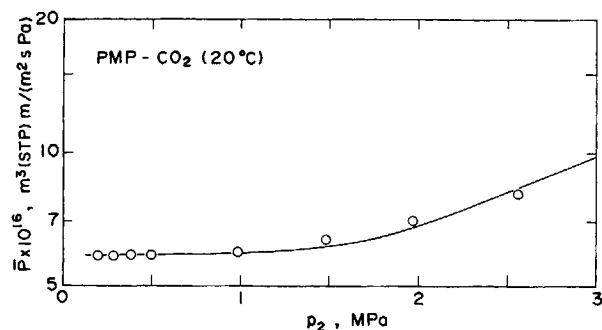


Figure 4 Pressure dependence of mean permeability coefficient for CO₂ in PMP membrane at 20°C. Comparison with the prediction by the proposed model.

pressures below ca. 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 CO₂ 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 CO₂ 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). The plasticization action to the rubbery polymer here emerges in the diffusion process rather than in the sorption process at gas pressures up to 2.5 MPa. The plasticization action in the glassy state of the polymer might come out as the depression of unrelaxed microvoids in the sorption process as well as in the diffusion one.

Figures 4 and 5 indicate the comparison of the observed pressure dependencies of the mean permeability coefficients for CO₂ in PMP at 20°C and in PS at 60 and 70°C with the predictions by eq. (17) combined with eq. (6). 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. (6), i.e., a combination of a gas-polymer-matrix model with the sorption theory of Mi et al.,² can interpret the trend of the pressure dependence of the mean permeability coefficient for CO₂.

CONCLUSION

To simulate the simultaneous deviation from both conventional dual-mode sorption and mobility

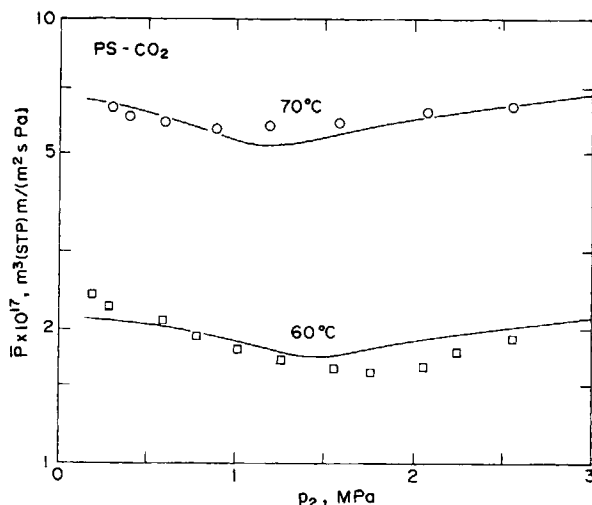


Figure 5 Pressure dependence of mean permeability coefficient for CO₂ in PS membrane at 60 and 70°C. Comparison with the prediction by the proposed model.

models, a gas-polymer-matrix model was combined with the sorption theory of Mi et al., where the glass transition temperature is depressed by a concentration of sorbed species of the plasticizing ability. For the systems of CO₂-poly-4-methyl-1-pentene membrane at 20°C and CO₂-polystyrene membrane at 60 and 70°C, the plasticization action in the glassy state of the polymers is brought about in the sorption process as the depression of unrelaxed microvoids and in the diffusion process. The sorption and permeation behavior influenced by the plasticization action of sorbed gas molecules can be simulated considerably well by the combined model proposed here.

NOMENCLATURE

- A parameter involved in Eq. (6) (K⁻¹)
- b Langmuir affinity constant (Pa⁻¹)
- C concentration of total sorbed species [m³(STP)/m³]

Table II Values of Parameters β and D_0 Involved in Eq. (15) for CO₂ in PMP and PS Membranes

Membrane	Temp (°C)	β [m ³ /m ³ (STP)]	$D_0 \times 10^{17}$ [m ² /s]
PMP	20	0.07	4.53
PS	60	0.04	0.301
PS	70	0.05	1.05

C_D	concentration of Henry's law species [$\text{m}^3(\text{STP})/\text{m}^3$]
C_g	glass transition concentration appearing in Eq. (2) [$\text{m}^3(\text{STP})/\text{m}^3$]
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 for plasticization by sorbed gas molecule [$\text{m}^3(\text{STP})/\text{m}^3$]
D	diffusion coefficient in membrane (m^2/s)
f	ratio of the plasticizing ability of Langmuir species to that of Henry's law species appearing in Eq. (5)
J	permeation flux [$\text{m}^3(\text{STP})/(\text{m}^2\text{s})$]
k_D	Henry's law constant [$\text{m}^3(\text{STP})/(\text{m}^3\text{Pa})$]
\bar{P}	mean permeability coefficient [$\text{m}^3(\text{STP})\text{m}/(\text{m}^2\text{sPa})$]
p	pressure of penetrant gas (Pa)
S_0	solubility coefficient in the limit of $p \rightarrow 0$ [$\text{m}^3(\text{STP})/(\text{m}^3\text{Pa})$]
T_g	glass transition temperature (K)
x	position coordinate in the net flux direction (m)
β	dissolved gas-polymer interaction parameter appearing in eqs. (10), (11), and (15) [$\text{m}^3/\text{m}^3(\text{STP})$]
δ	thickness of membrane (m)
σ	parameter characterizing the concentration dependence of Henry's law constant appearing in Eq. (2) [$\text{m}^3/(\text{m}^3(\text{STP}))$]

Subscripts

D	Henry's law mode
H	Langmuir mode

s	steady-state
0	zero concentration state
1	downstream surface
2	upstream surface

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