NOTE

TRANSPORT PHENOMENA IN GAS PERMEATION THROUGH GLASSY POLYMER MEMBRANES WITH CONCENTRATION-DEPENDENT SORPTION AND DIFFUSION PARAMETERS

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Abstract—The modified dual-mode mobility model for permeation of a gas in glassy polymer membranes was combined with the extended dual-mode sorption model to take account of the plasticization effect of sorbed gas molecules on both sorption and diffusion processes. The combined model was further simplified by the introduction of a concentration of the mobile gas species. However, the observed pressure dependence of mean permeability coefficients of carbon dioxide in methylmethacrylate-n-butyl acrylate copolymer and polymethylmethacrylate films at 30°C and also that of oxygen in a polycarbonate film at 50°C and 60°C showed that a plasticization action of sorbed gas species has an influence on the diffusion process rather than on the sorption process, that is, were simulated by the modified dual-mode mobility model combined with the conventional dual-mode sorption model.

INTRODUCTION

The dual-mode sorption and mobility model has been widely used to describe sorption and diffusion behavior of a gas in glassy polymer membranes. The dual-mode sorption model postulates that molecules are sorbed in a polymer as Henry's law species or Langmuir species. The dual-mode mobility model assumes that these two species are in local equilibrium with each other during diffusion.

In the original dual-mode sorption model, Henry's law and Langmuir capacity constants are assumed to be constant, irrespectively of the sorbed amount. 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. They showed clearly in sorption isotherms in several systems of CO_2-glassy polymer that the plasticization of 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 temperature of the pure polymer [1-3].

Zhou and Stern [4] modified the dual-mode mobility model to polymer-gas systems in which sorbed

gas molecules plasticizes the polymer. In their model, the diffusivities of dissolved and adsorbed species depend on the concentration of the corresponding species, while the dual-mode sorption parameters are not affected by the concentration of sorbed species. The observed pressure dependences for pure CO_2 in homogeneous membranes of cellulose triacetate and methylmethacrylate and n-butyl acrylate copolymer could be simulated well by this modified model [5]. Further, the experimental results on the pressure dependence of mean permeability coefficients for CO_2-CH_4 equimolar mixture in the same membranes were predicted satisfactorily by an extension to binary gas mixture of the modified mobility model for a single gas [5].

Currently, there have appeared no experimental results available on the plasticization action of the sorbed gas exerting on both sorption and diffusion processes simultaneously. But, when the temperatures for sorption and permeation experiments are not so high as the glass-transition temperature of the pure polymer, the plasticization effect of the sorbed gas possibly appears in both the sorption and diffusion processes simultaneously in the moderate pressure range.

In the present work, we attempted to combine the modified dual-mode mobility model [4] with the extended dual-mode sorption model [1] to take account the plasticization effect of sorbed gas molecules on both sorption and diffusion processes. This combined

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model was further simplified by introduction of the concept of a concentration of the mobile gas species.

MODIFIED DUAL-MODE MODEL FOR SINGLE GAS PERMEATION

The problem considered here is that of sorption and diffusion for glassy polymer-gas systems in which gas molecules plasticize the polymer matrix. According to the extended dual-mode sorption model proposed by Kamiya et al. [1], the concentration of sorbed gas is written as

$$C = C_D + C_H \tag{1}$$

where $C_D = [k_D \exp(\sigma C^*)]p \tag{2}$

$$C_H = \frac{C'_{H0}bp(1 - C^*/C_g)}{1 + bp} \tag{3}$$

C_D and C_H are the concentration of dissolved (Henry's law) and that of adsorbed (Langmuir) species, respectively. k_D is a solubility coefficient and b is a kinetic factor (the "site affinity" constant). In the Eq. (3), C'_{H0} and C_g refer to the Langmuir capacity constant in the limit of p→0 and the glass transition concentration, respectively, and σ is the parameter characterizing the concentration dependence of C_D/p introduced by Suwandi and Stern [6]. This was employed for analyzing sorption of water vapor in polyacrylonitrile by Mauze and Stern [7]. C* denotes the effective concentration for plasticization by sorbed gas defined as

$$C^* = C_D + fC_H \tag{4}$$

where f is the ratio of the plasticizing ability of Langmuir species to that of Henry's law species [1]. When C* approaches C_g, the concentration of Langmuir species becomes equal to zero according to Eq. (3). That is, the glass transition is brought out by the sorbed gas at temperatures below the glass-transition temperature of the pure polymer.

According to the modified dual-mode mobility model proposed by Zhou and Stern [4], the diffusivities of dissolved and adsorbed species (D_D and D_H) should be dependent on the concentration of the corresponding species:

$$D_D = D_{D0} \exp(\beta_D C_D) \tag{5}$$

$$D_H = D_{H0} \exp(\beta_H C_H) \tag{6}$$

where D_{D0} and D_{H0} are the mutual diffusion coefficients in the limits C_D→0 and C_H→0, respectively; β_D and β_H are emperical constants that depend only on the nature of the penetrant/polymer system and

the temperature and characterize the effects of plasticization on penetrant transport in the Henry's law and Langmuir domains, respectively.

The diffusion flux, J, therein can be written as

$$J = -D_{D0} \exp(\beta_D C_D)\frac{\partial C_D}{\partial x} - D_{H0} \exp(\beta_H C_H)\frac{\partial C_H}{\partial x} \tag{7}$$

With J constant at the steady state, the integration from the upstream side (subscrpt 2) to the downstream side (subscript 1) of the membrane leads to

$$J\delta = \frac{D_{D0}}{\beta_D} [\exp(\beta_D C_{D2}) - \exp(\beta_D C_{D1})]$$
$$+ \frac{D_{H0}}{\beta_H} [\exp(\beta_H C_{H2}) - \exp(\beta_H C_{H1})] \tag{8}$$

where δ is the thickness of membrane.

Thus, the mean permeability coefficient, $\overline{P}$, defined by $J\delta/(p_2 - p_1)$, is derived as

$$\overline{P} = \frac{D_{D0}}{\beta_D(p_2 - p_1)} [\exp(\beta_D C_{D2}) - \exp(\beta_D C_{D1})]$$
$$+ \frac{D_{H0}}{\beta_H(p_2 - p_1)} [\exp(\beta_H C_{H2}) - \exp(\beta_H C_{H1})] \tag{9}$$

In particular, when p_1→0, the above equation reduces to

$$\overline{P} = \frac{D_{D0}}{\beta_{D2}p_2}[\exp(\beta_D C_{D2}) - 1] + \frac{D_{H0}}{\beta_H p_2}[\exp(\beta_H C_{H2}) - 1] \tag{10}$$

In reality Eq. (9) based on a modified dual-mode model (i.e., combination of extended dual-mode sorption model and modified dual-mode mobility model) has the same form as that based on a modified dual-mode mobility model (i.e., combination of conventional dual-mode sorption model and modified dual-mode mobility model), but it should be noted that C_{D2} and C_{H2} must be determined by a trial and error procedure from Eq. (2) to (4), according to an extended dual-mode sorption model.

The permeation model proposed above, which results from the combination of the extended dual-sorption model and the modified dual-mode mobility model, is regarded as one of the most elaborate model for gas permeation in glassy polymer membranes. The proposed model should be operative in the moderate pressure region, when the temperature of permeation runs is not so high as the glass-transition temperature of the pure, i.e., penetrant free, polymer.

SIMPLIFICATION OF MODIFIED DUAL-MODE MODEL

Stern and Saxena [8] derived an integrated model for permeation of a gas in glassy polymers by assuming the concentration-dependent diffusivity, D (C_m), of the type

$$D(C_m) = D_o \exp(\beta C_m) \qquad (11)$$

Here, C_m refers to the concentration of the mobile gas species defined as

$$C_m = C_D + FC_H \qquad (12)$$

where F is a fraction of C_H which has the same mobility as C_D.

According to their integrated model combined with the extended dual-mode sorption model, the diffusion flux can be given as

$$J = -D_o \exp(\beta C_m)\frac{\partial C_m}{\partial x} \qquad (13)$$

In conjunction with the extended dual-mode sorption model [1], C_D and C_H involved in C_m can be given by Eqs. (2) and (3), respectively. Furthermore, if the effective concentration (C*) is assumed to be equal to C_m (i.e. f=F), C_D and C_H are written as follows:

$$C_D = [k_D \exp(\sigma C_m)]p \qquad (14)$$

$$C_H = \frac{C'_{H0} \ bp(1 - C_m/C_g)}{1 + bp} \qquad (15)$$

Mauze and Stern [7] proposed a modified dual-mode model, wherein Eq. (14) was combined with a modified sorption isotherm:

$$C = [k_D \exp(\sigma C)]p + C'_H \ bp/(1 + bp) \qquad (16)$$

The above equation suggests that the plasticization action of the sorbed gas exerts only on the Henry's law mode.

From Eq. (13), the mean permeability coefficient is derived as

$$\overline{P} = \frac{D_0}{\beta(p_2 - p_1)}[\exp(\beta C_{m2}) - \exp(\beta C_{m1})] \qquad (17)$$

When the downstream pressure approaches zero, Eq. (17) reduces to

$$\overline{P} = \frac{D_0}{\beta p_2}[\exp(\beta C_{m2}) - 1] \qquad (18)$$

Also, C_{m2} must be calculated by a trial and error procedure to Eqs. (12), (13) and (15).

EXAMPLES

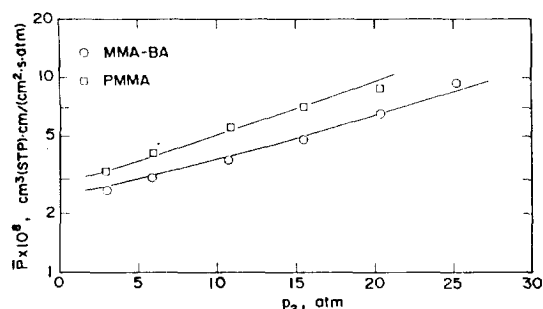It should be kept in mind that the permeability ex-

Fig. 1. Mean permeability coefficients for carbon dioxide in MMA-BA copolymer and PMMA films as a function of upstream pressure at 30°C. The solid curves represent the results calculated by Eq. (20).

pressions, Eqs. (9) and (17), have such many parameters as nine and seven, respectively. Five sorption parameters k_D, σ, b, C'_H and f can be estimated from the sorption equilibrium data, whereas four or two diffusion parameters D_{D0}, D_{H0}, β_D and β_H or D_0 and β (F=f) can be determined from independent permeability data. Currently, the permeability data justifying the usefulness of these expressions have not been available. Because the pressure range bringing out the plasticization effect of the sorbed gas on the sorption equilibria surpassed that of permeation runs. But we have the permeability data justifying the usefulness of those with $\sigma \to 0$ and $C^*/C_g \to 0$ in Eq. (1), the modified dual-mode model proposed by Zhou and Stern [4] (i.e. Eq. (9) which was derived by Sada et al. [5]) is operative.

Fig. 1 shows the mean permeability coefficients of carbon dioxide in methylmethacrylate-butyl acrylate (MMA-BA) copolymer film at 30°C [9] as a function of the upstream pressure as circles. The permeability is found to increase monotonously with increasing the upstream pressure. The sorption isotherm of this system at the same temperature has been known to be described well by the conventional dual-mode sorption model [5], viz.

$$C = k_D p + \frac{C'_H \ bp}{1 + bp} \qquad (19)$$

The values of the dual-mode sorption parameters have been determined to be $k_D = 1.30$ cm^3 (STP)/(cm^3 atm), b=0.623 atm^{-1} and $C'_H = 12.2$ cm^3 (STP)/cm^3 [5]. When $\sigma \to 0$, $C^*/C_g \to 0$ and $D_{H0} \to 0$, Eq. (9) can be simplified to

$$\overline{P} = \frac{D_{D0}}{\beta_D(p_2 - p_1)}[\exp(\beta_D k_D p_2) - \exp(\beta_D k_D p_1)] \qquad (20)$$
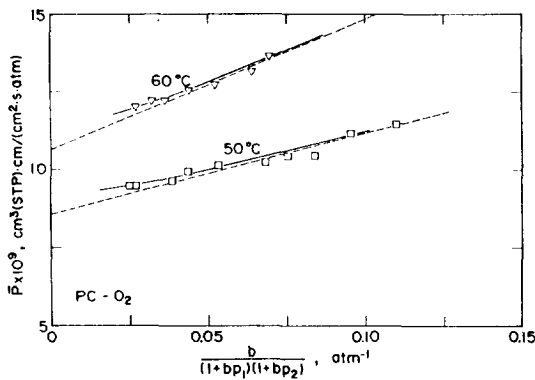
Fig. 2. Pressure dependence of mean permeability coefficient for oxygen in polycarbonate film at 50°C and 60°C and comparison with Eq. (21). The solid curves represent the results calculated by Eq. (21), while the broken lines represent the results calculated by the conventional dual-mode mobility model.

The solid curve fitting to circles in Fig. 1 represents the result calculated by Eq. (20) with adjusted values: $D_{D0} = 1.82 \times 10^{-8}$ cm^2/s and $\beta_D = 0.065$. In the same figure, the mean permeability coefficients for the same gas in polymethylmethacrylate(PMMA) film at 30°C have also been plotted against the upstream pressure as squares. The solid curve fitting to the squares represents the result calculated by Eq. (20), wherein $D_{D0} = 2.67 \times 10^{-8}$ cm^2/s, $\beta_D = 0.108$, and the value of k_D at 30°C was assumed to be equal to the value at 35°C measured by Sanders et al. [10] ($k_D = 1.015$ cm^3(STP)/ (cm^3 atm) at 35°C ; b=0.243 atm^{-1} and $C_H' = 11.856$ cm^3(STP)/cm^3 at 35°C, both of which are not used in this calculation).

Fig. 2 demonstrates the pressure dependence of the mean permeability coefficient of oxygen in polycarbonate film at 50°C and 60°C [11], where the mean permeability coefficients are plotted on the basis of a conventional dual-mode mobility model derived by gradients of concentration. The values of the conventional dual-mode sorption parameters for this system are listed in Table 1. It is apparent from Fig. 2 that the permeabilities at relatively high upstream pressures

deviate a little bit from the dual-mode model as presented by broken lines. Then the experimental data on the mean permeability coefficients fitted a simplified form of Eq. (17).

The simplified form is derived as follows: from Eq. (17) with σ and C_m/C_g set equal to zero, the mean permeability coefficient can be derived approximately as

$$\bar{P} \cong D_0 \left\{ k_D + \frac{FC'_{H0} \; b}{(1+bp_1)(1+bp_2)} \right\} \{1 + \beta(C_{m1}+C_{m2})\} \quad (21)$$

where β must be much smaller than 1. The broken lines representing Eq. (21) with $\beta = 0$ were calculated by using diffusion parameters D_0 and F along with the conventional dual-mode sorption parameters listed in Table 1. Fig. 2 also reveals the comparison between these. The value of the parameter β representing the plasticization action induced by sorbed gas can be determined to be 0.03, from the solid curve calculated by Eq. (21).

CONCLUSION

The modified dual-mode mobility model was formally combined with the extended dual-mode sorption model. Existing permeability data for a single gas in which the sorbed gas molecules plasticized the polymers, showed an influence on the diffusion process rather than on the sorption process.

NOMENCLATURE

b   : Langmuir affinity constant [atm^{-1}]

C   : total sorbed concentration of penetrant [cm^3 (STP)/cm^3]

C_D : concentration of Henry's law population [cm^3 (STP)/cm^3]

C_g : glass-transition concentration in Eq. (3) [cm^3 (STP)/cm^3]

C_H : concentration of Langmuir population [cm^3 (STP) /cm^3]

C'_H : Langmuir capacity constant [cm^3 (STP)/cm^3]

C_m : concentration of mobile species defined by Eq. (13) [cm^3 (STP)/cm^3]

Table 1. Sorption and diffusion parameters for oxygen in polycarbonate film

Temp. (°C)	k_D [cm^3 (STP)/(cm^3 atm)]	b (atm^{-1})	C'_H [cm^3 (STP)/cm^3]	$D_0 \times 10^7$ (cm^2/s)	F (-)
50	0.030	0.40	0.60	5.91	0.152
60	0.018	0.20	0.25	8.58	0.284

Note: $D_0 = D_{D0}$

C* : effective concentration for plasticization by sorbed gas [cm^3 (STP)/cm^3]

D : diffusion coefficient in membrane [cm^2/s]

F : fraction of C_H which has the same mobility as C_D

f : ratio of the plasticizing ability of Langmuir species to that of Henry's law species in Eq. (4)

k_D : Henry's law constant [cm^3 (STP)/(cm^3 atm)]

$\overline{P}$: mean permeability coefficient [cm^3 (STP) cm/(cm^2 s atm]

p : pressure of penetrant gas [atm]

x : position coordinate in the net flux direction [cm]

δ : thickness of membrane [cm]

σ : parameter characterizing the concentration dependence of Henry's law constant in Eq. (2) [cm^3/cm^3 (STP)]

β : concentration-dependence parameter in Eq. (5), (6) and (11) [cm^3 (STP)/cm^3]

Subscripts

D : Henry's law mode

H : Langmuir mode

0 : zero concentration state

1 : downstream surface

2 : upstream surface

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