# Sorption and Diffusion of Carbon Dioxide in Polyimide Films

E. SADA, H. KUMAZAWA, and P. XU, *Department of Chemical Engineering, Kyoto University, Kyoto 606, Japan*

## Synopsis

The sorption isotherms of carbon dioxide in a polyimide film sample were measured by a pressure decay method at 30, 40, 50, and 60°C and pressures up to 1.7 MPa. The mean permeability coefficients at the same temperatures were measured by a variable volume method at applied upstream pressures up to 3 MPa. The sorption equilibria at these temperatures were found to be well described in terms of a dual-mode sorption model. The pressure dependences of the mean permeability coefficients at these four levels of temperatures did not satisfactorily follow a dual-mode mobility model, but could be well simulated by a modified mobility model that both the Henry's law ($D$) and Langmuir ($H$) populations execute four kinds of diffusive movements such as $D \to D$, $D \to H$, $H \to D$, and $H \to H$. The diffusion coefficients of $D \to D$, $D \to H$, and combined $H \to H$ and $H \to D$ steps were determined by comparing the experimental permeability data with those predicted via this modified mobility model. The temperature dependences of such diffusion coefficients were consistent with Arrhenius-type equations within the covered temperatures.

## INTRODUCTION

The sorption of gases and vapors in glassy polymers is generally more complex than in rubbery polymers. Since Barrer et al.[1] proposed first a dual-mode sorption model for an equilibrium of sorption for a gas in a glassy polymer, the sorption equilibria have been measured for many gas–glassy polymer systems and have been described in terms of such a sorption model. In the dual-mode sorption model, penetrant molecules are retained in the polymer in two distinct ways, i.e., Henry's law dissolution and Langmuir adsorption. Currently, it is no exaggeration to say that this dual-mode concept at sorption equilibrium has been well established, whereas a parallel treatment for transport of both dissolved and adsorbed molecular populations in glassy polymers has not been well established yet. The most important model to meet such an object is so-called dual-mode mobility model[2,3] that both the populations execute diffusive movements with different mobilities. But the dual-mode mobility model has not been tested in many gas–glassy polymer systems. The applicability of this model has not been confirmed yet.

By considering such a situation, in this work, sorption and permeation of carbon dioxide for a commercially available polyimide film are measured to especially discuss the mechanism of diffusion of a gas in glassy polymers. First, the sorption isotherms of carbon dioxide in a polyimide film sample were measured at 30, 40, 50, and 60°C and pressures up to 1.7 MPa, and the dual-mode sorption parameters were determined. Secondly, permeability coefficients were measured for upstream pressures up to 3 MPa at the same

temperatures. In conjunction with measured sorption parameters, a gas diffusion mechanism has been discussed by comparing the present permeability data with the existing transport models.

A glassy polyimide used in this work is an important engineering plastic and has an excellent property of exceptional chemical and thermal stability. Thus, the glassy polyimide has been currently regarded as one of the most promising materials for preparing gas separation membranes.

## THEORETICAL BACKGROUND

The sorption isotherms of gases in glassy polymers have been found to be satisfactorily described by a so-called dual-mode sorption model, which postulates a combination of Langmuir-type adsorption in preexisting microvoids plus Henry's law dissolution in the polymer matrix.[1] Quantitatively, this may be described by a sum of Henry's law and Langmuir terms, viz.,

$$C = C_D + C_H = k_D p + C'_H b p / (1 + bp) \tag{1}$$

The two sorbed populations, which are termed Henry's law and Langmuir populations, respectively, can execute diffusive movements with different mobilities, while being at local equilibrium with each other. This approach has been called a dual-mode mobility or transport model. There are two kinds of fluxes derived from the dual-mode mobility driven by the gradients of chemical potential and concentration.

The diffusion flux in terms of chemical potential gradients has been presented by Petropoulos,[2] viz.,

$$J = -k_D D_D \left(1 + \frac{FK}{1 + bf}\right) \frac{\partial f}{\partial x} \tag{2}$$

where the fugacity is used because the chemical potential should be expressed in terms of activity or fugacity. The mean permeability coefficient, which is defined by

$$\overline{P} = J_s l / (f_2 - f_1) \tag{3}$$

is given as

$$\overline{P} = k_D D_D + \frac{C'_H D_H}{f_2 - f_1} \ln \frac{1 + bf_2}{1 + bf_1} \tag{4}$$

One assumes ideal gas behavior for simplicity, so that the fugacity is replaced by the pressure. Thus, eq. (4) reduces to

$$\overline{P} = k_D D_D + \frac{C'_H D_H}{p_2 - p_1} \ln \frac{1 + bp_2}{1 + bp_1} \tag{5}$$

On the other hand, the diffusion flux in terms of concentration gradients has been given by Paul and Koros,[3] viz.,

$$J = -D_D\frac{\partial C_D}{\partial x} - D_H\frac{\partial C_H}{\partial x} \tag{6}$$

$$= -D_D\left[1 + \frac{FK}{(1 + \alpha C_D)^2}\right]\frac{\partial C_D}{\partial x} \tag{7}$$

where the latter form is derived by substituting the assumption of local equilibrium between the two modes.

The mean permeability coefficient defined by

$$\bar{P} = J_s l/(p_2 - p_1) \tag{8}$$

with $f$ replaced by $p$ in eq. (2), is derived as follows:

$$\bar{P} = k_D D_D + \frac{C_H' b D_H}{(1 + bp_1)(1 + bp_2)} \tag{9}$$

If the dual-mode mobility model driven by the gradients of chemical potential is operative, then the mean permeability coefficient $\bar{P}$ should be linear to the term

$$\frac{1}{f_2 - f_1}\ln\frac{1 + bf_2}{1 + bf_1} \quad \text{or} \quad \frac{1}{p_2 - p_1}\ln\frac{1 + bp_2}{1 + bp_1}$$

From the slope and intercept of the straight line, the diffusion coefficients of Henry's law and Langmuir modes can be determined by using the dual-mode sorption parameters.

On the other hand, if the dual-mode mobility model driven by the gradients of concentration is valid, the relationship between the mean permeability coefficient $\bar{P}$ and the term $b/(1 + bp_1)(1 + bp_2)$ should give a straight line. Similarly, from the slope and intercept of the straight line, the diffusion coefficients of two respective modes can be determined.

## EXPERIMENT

Equilibrium sorption of carbon dioxide by a polyimide film sample was measured by a pressure decay method. The sorption cell is similar to one designed by Koros et al.[4] The pressure in the sorption cell was continuously measured by a pressure transducer. The apparatus for permeability measurements is similar to the variable volume method employed by Stern et al.[5] Carbon dioxide to be permeated was fed into the high-pressure side, while the low-pressure side was filled with the same gas at 0.101 MPa. Hence, the downstream pressure is always kept constant at 0.101 MPa. The volumetric flow rate through the membrane to the low-pressure side was measured by observing the displacement of a small amount of 1-propanol in the capillary

tube connected to the low-pressure side. The mean permeability coefficient was determined by this steady state permeation rate. The permeation area in this cell was 19.6 cm$^2$.

The Upilex polyimide film samples used in the present work were kindly supplied by Ube Industries, Ltd., Japan. The structure is
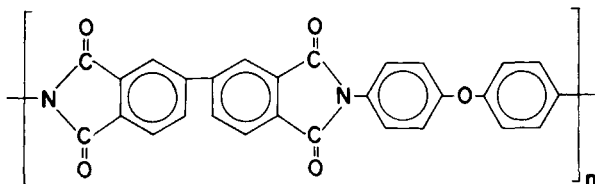


The glass transition has been reported to be 285°C by Ube Industry, Ltd. The thickness of the film used for permeation and sorption measurements was 21.4 $\mu$m. Sorption runs were carried out at 30, 40, 50, and 60°C and pressures up to 1.7 MPa. Permeation runs were made at the same temperatures and upstream pressure up to 3 MPa.

## EXPERIMENTAL RESULTS AND DISCUSSION

### Sorption Equilibria

The measured sorption isotherms for carbon dioxide in polyimide film at 30, 40, 50, and 60°C are shown in Figure 1. Each isotherm exhibits a similar upward convex pattern observed for the typical glassy polymers.[6,7] Likewise, the behavior could be simulated by a so-called dual-mode sorption model, viz., eq. (1). The dual-mode sorption parameters appearing in eq. (1) were determined by using the nonlinear least square algorithm and are listed in Table
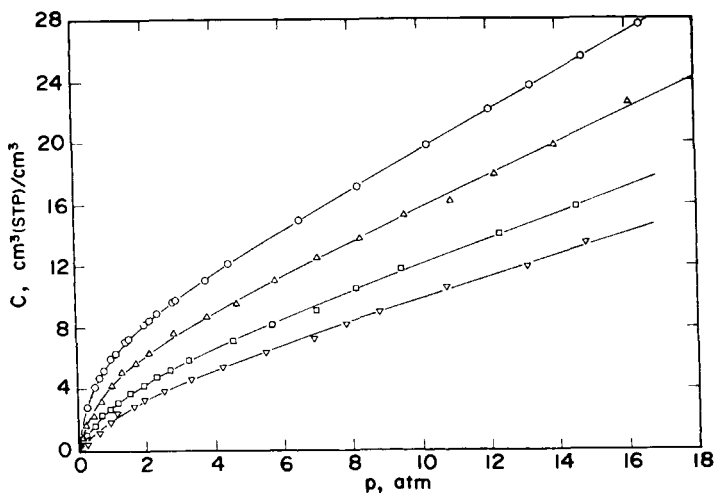


Fig. 1. Sorption isotherms for carbon dioxide in polyimide film samples at different temperatures (°C): (○) 30; (△) 40; (□) 50; (▽) 60.

TABLE I
Dual-Mode Sorption Parameters for CO$_2$–Polyimide

| Temp. (°C) | $k_D$ [cm$^3$ (STP)/cm$^3$ atm] | $b$ (atm$^{-1}$) | $C'_H$ [cm$^3$ (STP)/cm$^3$] | $K$ ($= C'_H b/k_D$) |
|---|---|---|---|---|
| | Parameters in eq. (1) using $p$ | | | |
| 30 | 1.24 | 1.70 | 7.39 | 10.13 |
| 40 | 1.04 | 1.23 | 5.67 | 6.71 |
| 50 | 0.817 | 0.865 | 4.27 | 4.52 |
| 60 | 0.692 | 0.635 | 3.34 | 3.05 |
| | Parameters in eq. (1) with $p$ replaced with $f$ | | | |
| 30 | 1.35 | 1.91 | 6.93 | 9.80 |
| 40 | 1.12 | 1.35 | 5.28 | 6.36 |
| 50 | 0.875 | 0.954 | 3.95 | 4.31 |
| 60 | 0.736 | 0.683 | 3.09 | 2.87 |

I. The solid curves in Figure 1 represent the calculated sorption isotherms by eq. (1) using these estimates. In Table I, the values of such dual-mode sorption parameters based on fugacity instead of pressure are also listed to use for testing the validity of dual-mode mobility model driven by chemical potential gradients.
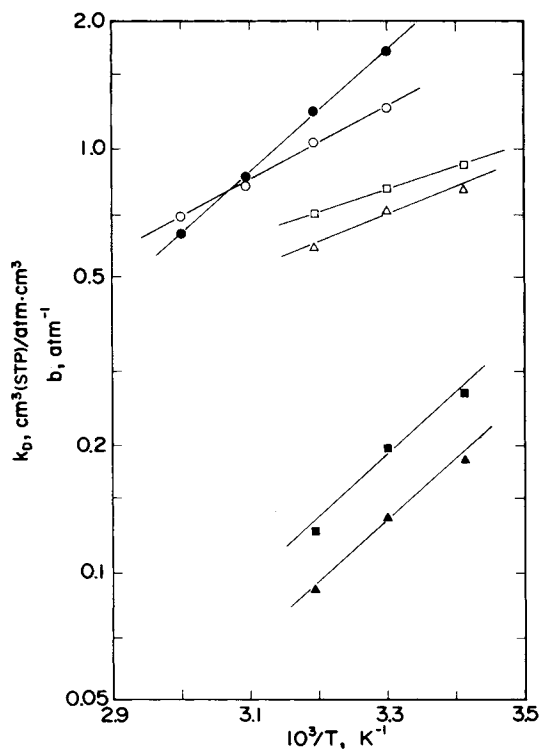


Fig. 2. Effect of temperature on Henry's law constant $k_D$ (○, □, △) and Langmuir affinity constant $b$ (●, ■, ▲) for carbon dioxide in various glassy polymers: (○, ●) PI; (□, ■) PC; (△, ▲) PS.
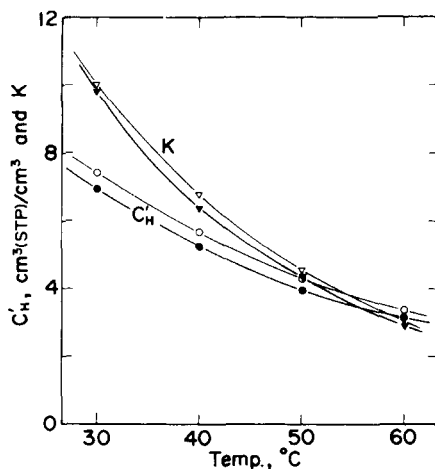
Fig. 3. Effect of temperature on Langmuir capacity constant for carbon–polyimide: (●, ▼) based on $f$.

The temperature dependences of the dual-mode sorption parameters using pressure are indicated in Figures 2 and 3. Figure 2 shows the van't Hoff plots of Henry's law constant $k_D$ and Langmuir affinity constant $b$. In the same figure, the corresponding parameters for carbon dioxide in polycarbonate (PC) and polystyrene (PS), which were reported by the present authors,[7] are also plotted. The enthalpy changes of gases held in Henry's law dissolution and Langmuir adsorption modes relative to the free gas standard state can be calculated from the slopes of van't Hoff plots of $k_D$ and $b$, respectively. The linearity of the van't Hoff plots indicates that the respective enthalpy changes of sorption are constant over the temperature range of these experiments. The enthalpy changes in the Henry's law ($\Delta H_D$) and Langmuir ($\Delta H_H$) modes are collectively listed in Table II. The larger enthalpy changes observed for the Langmuir mode relative to the Henry's law mode are reasonable by considering that sorption in the Langmuir mode occurs in preexisting microvoids. The enthalpy change of Langmuir adsorption mode for the present $CO_2$–polyimide (PI) system is found to be close to for such glassy polymers as polycarbonate (PC) and polystyrene (PS).

The Langmuir capacity should be proportional to the unrelaxed microvoid volume in a glassy polymer, and, accordingly, the Langmuir capacity constant $C_H'$ must approach zero at a glass transition temperature of the polymer. In

TABLE II
Enthalpy Changes in Henry's Law Dissolution and Langmuir Adsorption Modes

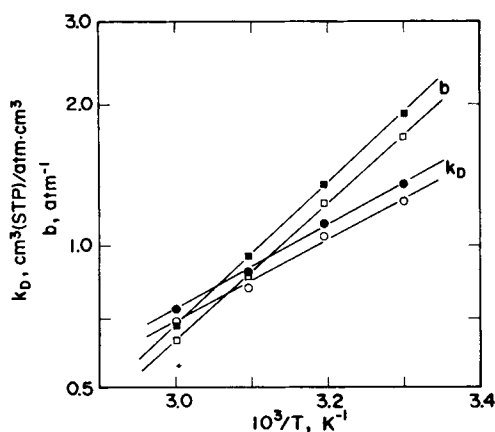| System | $\Delta H_D$ (kJ/mol) | $\Delta H_H$ (kJ/mol) |
|---|---|---|
| PI–$CO_2$ | −16.6 | −27.9 |
| PI–$CO_2$[a] | −15.9 | −29.0 |
| PC–$CO_2$[7] | −9.9 | −28.7 |
| PS–$CO_2$[7] | −11.2 | −26.5 |

[a] Based on fugacity.

Fig. 4. Effect of temperature on Henry's law constants and Langmuir affinity constants based on pressure ($\bigcirc$, $\square$) and fugacity ($\bullet$, $\blacksquare$) for carbon dioxide–polyimide.

Figure 3, the Langmuir capacity constants for CO$_2$–PI were plotted as a function of temperature, along with the corresponding constants using fugacity. As the temperature goes up, the Langmuir capacity constant is shown to decrease monotonically. The covered temperatures are very low as compared to the glass transition temperature of the present PI sample (285°C). Hence, Figure 3 does not show clearly that the Langmuir capacity constants monotonically reduces to zero as the glass transition temperature is approached.

The Henry's law and Langmuir affinity constants with pressure replaced by fugacity were shown as van't Hoff plots in Figure 4, along with these constants using pressure. The enthalpy changes in the Henry's law and Langmuir modes using fugacity are found to be very close to those using pressure as listed in Table II.

## Permeabilities

The experimental results of mean permeability coefficients of carbon dioxide through the polyimide film were indicated as a function of upstream pressure $p_2$ in Figure 5. The permeability coefficients at every temperature were found to exhibit pressure dependence, characteristic of glassy polymers. Then, it was checked whether the observed pressure dependence of the mean permeability coefficients obey the dual-mode mobility models driven by gradients of chemical potential and concentration or not.

First, the mean permeability coefficient data at every temperature were plotted on the basis of eq. (5) in Figure 6. The value of Langmuir affinity constant required for calculation of the abscissa has been shown in Table I. The plots at 30 and 40°C gave essentially straight lines, but those at 50 and 60°C deviated from straight lines. Exactly, the chemical potential should be expressed using the fugacity in place of pressure. To check the applicability of the dual-mode mobility model driven by gradients of chemical potential using the fugacity, the mean permeability coefficient data were further plotted on the basis of eq. (4) in Figure 7. The plots at 50 and 60°C still deviated from straight lines.
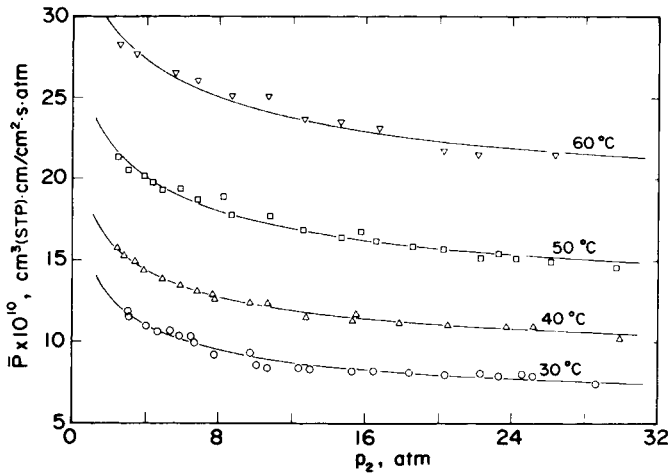
Fig. 5. Effect of pressure on mean permeability coefficient of carbon dioxide in polyimide film at different temperatures.

Secondly, to test the applicability of the dual-mode mobility model driven by gradients of concentration, the same permeability data were plotted on the basis of eq. (9) in Figure 8. The plots here did not give straight lines at all of the temperatures covered. The deviation from the linearity becomes large specifically at high applied pressures. Also, the deviation from the linearity even at 30 and 40°C is found to be considerable, though the absolute values of the deviation look small. Anyway, it was concluded that the mean permeability data at all of temperatures and pressures covered here could not be predicted by the dual-mode mobility models based on gradients of chemical potential as well as concentration.
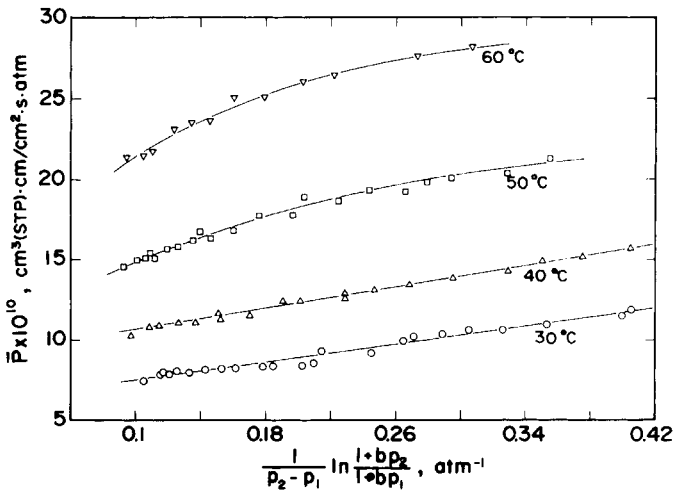


Fig. 6. Test of dual-mode mobility model based on gradients of chemical potential using pressure.
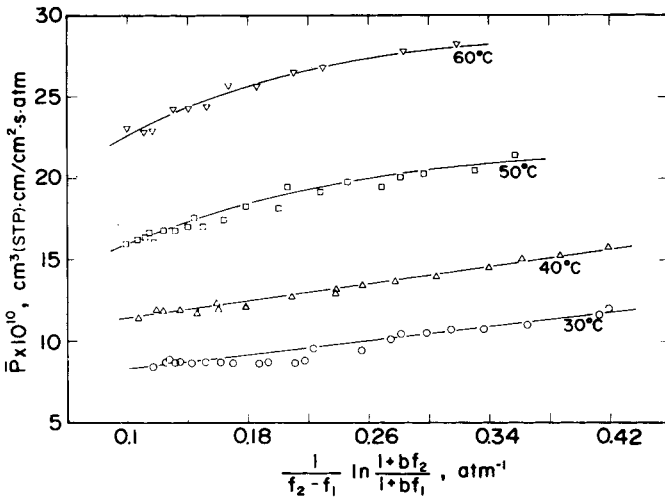
Fig. 7.   Test of dual-mode mobility model based on gradients of chemical potential using fugacity.

The dual-mode mobility model undoubtedly incorporates primary diffusive movements of Henry's law and Langmuir populations, but does not include diffusive movement of the Henry's law mode to the Langmuir mode. If two sorbed populations in the Henry's law and Langmuir modes designated $D$ and $H$, respectively, then four kinds of diffusive movements are basically possible: diffusive movements within the two modes ($D \to D$ and $H \to H$) and between the modes ($D \to H$ and $H \to D$). The total diffusion flux could then be given by summing the contribution of each diffusion step, viz.,

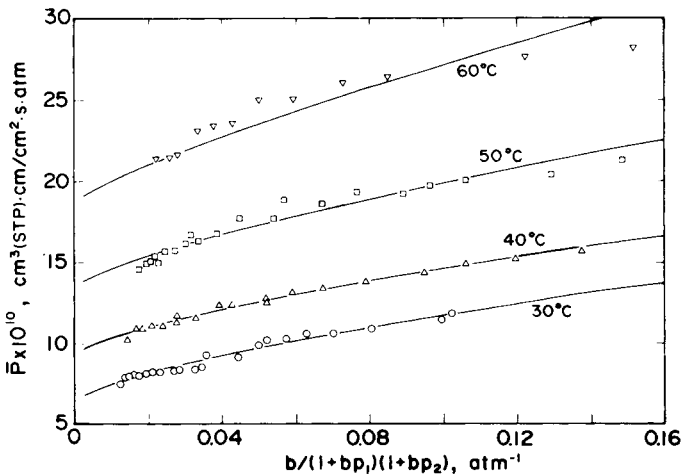$$J = J_{DD} + J_{HD} + J_{DH} + J_{HH} \tag{10}$$



Fig. 8.   Test of dual-mode mobility model based on gradients of concentration and comparison with Barrer's suggestion.

Recently, Barrer[8] theoretically derived the flux expression in terms of the concentration gradients for each diffusion step. The total diffusion flux can be written as

$$J = -D_{DD}\frac{\partial C_D}{\partial x} - D_{HD}\frac{\partial C_H}{\partial x} - D_{DH}\left[\frac{\partial C_D}{\partial x}\left(1 - \frac{C_H}{C_H'}\right) + \frac{C_H}{C_H'}\frac{\partial C_H}{\partial x}\right)\right]$$

$$- D_{HH}\frac{\partial C_H}{\partial x} \tag{11}$$

After some rearrangement using the assumption of local equilibrium between the two modes and integrating the resultant equation over $C_D$ from $C_{D_1}$ to $C_{D_2}$ with $J$ and all coefficients constant, the mean permeability coefficient can be derived as follows[7]:

$$\overline{P} = k_D D_{DD} + \frac{2k_D D_{DH}}{b(p_2 - p_1)}\ln\frac{1 + bp_2}{1 + bp_1}$$

$$+ \frac{C_H'b(D_{HH} + D_{HD}) - k_D D_{DH}}{(1 + bp_1)(1 + bp_2)} \tag{12}$$

The permeability data which did not obey the dual-mode mobility models, as shown in Figures 6–8, were compared with eq. (12). The values of diffusivities $D_{DD}$, $D_{DH}$, and $(D_{HH} + D_{HD})$ were determined by using the nonlinear least-squares method at 30°C and at the other temperatures were determined by comparing the experimental permeability data with those predicted by eq. (12). They were listed in Table III. As suggested in eq. (12), the values of $D_{HH}$ and $D_{HD}$ cannot be evaluated separately; hence the value of $(D_{HH} + D_{HD})$ was evaluated by such data processing. The solid curves in Figures 5 and 8 represent the calculated relationships by eq. (12) with estimates of diffusivities listed in Table III, and at every temperature are in good agreement with experimental points over the whole range of pressures.

Figure 9 indicates the temperature dependences of the derived diffusion coefficients as Arrhenius plots. The diffusivities, $D_{DD}$, $D_{DH}$, and $D_{HH} + D_{HD}$, are found to follow Arrhenius-type relations in the range of covered temperatures. The values of $D_{DH}$, which reflect the deviation from the dual-mode mobility model, were found to exhibit very weakly dependent on temperature. The dissolved species basically has a potential of diffusive movements to the

TABLE III
Diffusion Parameters for $CO_2$–Polyimide

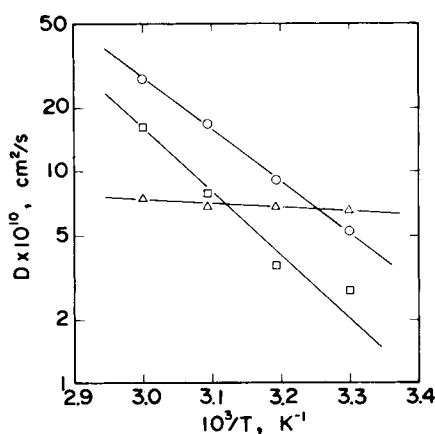| Temp. (°C) | $D_{DD} \times 10^{10}$ (cm²/s) | $D_{DH} \times 10^{10}$ (cm²/s) | $(D_{HH} + D_{HD}) \times 10^{10}$ (cm²/s) | $F$ $[= (D_{HH} + D_{HD})/D_{DD}]$ |
|---|---|---|---|---|
| 30 | 5.18 | 6.45 | 2.75 | 0.59 |
| 40 | 8.96 | 6.72 | 3.55 | 0.47 |
| 50 | 16.6 | 6.74 | 7.85 | 0.40 |
| 60 | 26.9 | 7.40 | 16.0 | 0.53 |

Fig. 9. Temperature dependence of diffusion coefficients in poly:mide film: (○) $D_{DD}$; (△) $D_{DH}$; (□) $D_{HH} + D_{HD}$.

TABLE IV
Activation Energies of Respective Diffusion Steps

| | |
|---|---|
| $D_{DD}$ | 47.2 kJ/mol |
| $D_{DH}$ | 3.5 kJ/mol |
| $D_{HH} + D_{HD}$ | 55.6 kJ/mol |

dissolved and adsorbed states, i.e., $D \rightarrow D$ and $D \rightarrow H$. Based on this observation, the value of $D_{DD}$ increases at a much faster rate than $D_{DH}$ with an increase in temperature. The dependence of dielectric constant at $10^3$ Hz of Upilex polyimide on temperature has been reported from Ube Industry, Ltd. Based on this report, the dielectric constants at 25 and 200°C are 3.5 and 3.2, respectively, and between these two temperatures, the dielectric constant gradually decreases with an increase in temperature. So there is not any secondary transition occurring around the covered temperatures. At this point, $D_{DH}$, thus, may be regarded as an adjustable parameter. The activation energies calculated from the plots in Figure 9 are given in Table IV. The larger activation energy observed for $D_{HH} + D_{HD}$ relative to that for $D_{DD}$ is reasonable due to the extra energy required to bring the gas in Langmuir adsorbed state up to the activated state required to proceed a diffusional jump.

The sorption and permeation behavior for carbon dioxide and methane in commercially available Kapton H polyimide at 60°C has been studied by Chern et al.[9] The sorption isotherm and the pressure dependence of mean permeability coefficient have been well simulated in terms of the dual-mode sorption and mobility model.

## CONCLUSION

The sorption isotherms for carbon dioxide in a polyimide film sample at 30, 40, 50, and 60°C were well described in terms of a dual-mode sorption model, and the dual-mode sorption parameters were determined by the nonlinear least-squares method. The temperature dependency of Henry's law and

Langmuir affinity constants were consistent with the van't Hoff equation. The Langmuir capacity constant was shown to decrease with an increase in temperature. The pressure dependences of the mean permeability coefficients at the same temperatures were not well simulated by the dual-mode mobility model, but could be satisfactorily described in terms of a modified mobility model that both the Henry's law and Langmuir populations execute four kinds of diffusive movements.

## APPENDIX: NOMENCLATURE

$b$     Langmuir affinity constant (atm$^{-1}$)
$C$     total sorbed concentration [cm$^3$ (STP)/cm$^3$]
$C_D$     concentration of Henry's law population [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$^3$]
$D$     diffusion coefficient in polymer film (cm$^2$/s)
$F$     mobility ratio defined by $D_H/D_D$ or $(D_{HH} + D_{HD})/D_{DD}$
$f$     fugacity (atm)
$J$     diffusion flux [cm$^3$ (STP)/(cm$^2$ s)]
$K$     $C'_H b/k_D$
$k_D$     Henry's law constant [cm$^3$ (STP)/(cm$^3$ atm)]
$l$     thickness of polymer film (cm)
$\bar{P}$     mean permeability coefficient [cm$^3$ (STP) cm/(cm$^2$ s atm)]
$p$     pressure (atm)
$R$     gas constant [kJ/(mol K)]
$T$     temperature (K)
$x$     distance coordinate (cm)

### Greek Symbols

$\alpha$     $b/k_D$
$\Delta H$     enthalpy change for gas sorption (kJ/mol)

### Subscripts

$D$     Henry's law mode
$DD$     within Henry's law mode
$DH$     from Henry's law mode to Langmuir mode
$H$     Langmuir mode
$HD$     from Langmuir mode to Henry's law mode
$HH$     within Langmuir mode
$s$     steady state
1     downstream of permeation cell
2     upstream of permeation cell

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