# Sorption and Diffusion of Water Vapor in Poly(ethylene terephthalate) Film

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**ABSTRACT:** The sorption and diffusion of water vapor in poly(ethylene terephthalate) (PET) film were measured by applying a thermogravimetric analyzer (TG-DTA), which customarily has been used to detect the weight loss of a sample with the increase of temperature under a given atmosphere. In this case, we detected the weight gain of PET film by sorption of water vapor under a given humidity at a constant temperature. Sorption-rate curves were successfully obtained in spite of the low solubility of PET film and the presence of Fickian-type curves. The solubility was better described according to the dual-mode sorption model. The diffusion coefficients were determined in their initial slopes by the short-time method. We found that the diffusion coefficient depended on vapor pressure. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 67–74, 2000

**Key words:** sorption; diffusion; water vapor; PET film; TG-DTA; dual-sorption model

## INTRODUCTION

It has been said that the mechanism of sorption and diffusion of water vapor in polymer films is more complex than that of the permanent gases. In the case of hydrophilic films, many investigations have provided useful information on the mechanism of plasticizing or clustering because of their relatively high solubility. On the other hand, the study of hydrophobic films such as polyethylene and poly(ethylene terephthalate) does not progress, because their solubility is low and it was not possible to measure the accurate sorption-rate curves, since errors were introduced by adsorption of water onto the glass outlet side of the equipment. Although many investigators have demonstrated interest in the behavior of hydrophobic glassy polymers, there have been relatively few studies. In this investigation, therefore, we tried to apply TG-DTA (thermal gravimeter–differential thermal analysis) and thus determined the accurate sorption rate curves of water in PET film. We also obtained the equilibrium sorption isotherms, the pressure dependency of solubility coefficients, and the diffusion coefficients. These data were analyzed by both the dual-sorption model and the dual-transport model.

## EXPERIMENTAL

### Sample

The PET (polyethylene terephthalate) film was used for the measurement. Figure 1 shows the structure of PET. This film was supplied by Mitsubishi Plastics Ltd. (Tokyo).[1] The density of the film is 1.400 g/cm$^3$ and the amorphous content is 0.48. DSC (Rigaku TAS 200 System; Rigaku Co., Tokyo) was used for the measurement of the
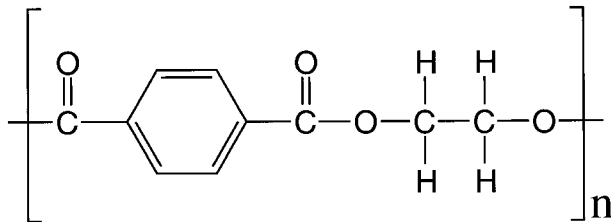
**Figure 1** Chemical structure of polyethylene terephthalate (PET).

glass-transition temperature ($T_g$). The temperature of the sample was raised 20 K min$^{-1}$ and it was determined that $T_g$ was 87°C and the melting point was about 260°C. The sample of the PET film was cut into strips of $2.0 \times 7.0$ cm$^2$, the thickness was $73.7 \times 10^{-4}$ cm.

Figure 2 shows the mounting method of PET film on the sample holder. The sample was rolled and fixed by the thin stainless wire (0.3 mm diameter). The top of it was set on the sample holder or the upper part of the balance. The humid mixed gas was supplied from the lower part of the sample chamber and was exhausted from the upper part, as shown in Figure 3.

## Apparatus

TG-DTA (Rigaku TAS 200 System; Rigaku Co., Tokyo)[2] was used for this purpose. Figure 3 is the schematic diagram of the water vapor sorption apparatus applying the TG-DTA, showing TG-DTA's laying pipes. Three different passages were prepared to introduce N$_2$ gas into TG-DTA equipment. N$_2$ gas was introduced from pipe laying and its purity is 0.4 ppm. The dry nitrogen gas supplied through valve 1 (V$_1$) serves as a curtain gas to protect the detector of the microbalance in the TG-DTA from water vapor. Water vapor was produced as high-humidity nitrogen by blowing dry nitrogen to wet wiping paper (Kimwipe; Kimberly-Clark Co., Tokyo) in a 1000-ml Erlenmeyer flask. The gas supplied through valve 2 (V$_2$) is dry nitrogen and through valve 3 (V$_3$) is high-humidity nitrogen. A prescribed humidity was obtained by controlling V$_2$ and V$_3$. The bulbs V$_1$, V$_2$, and V$_3$ are constituted with flow meters, respectively. The flow meters kept the constant humidity of the mixed gas within the sample chamber.

Figure 4 shows the passage of valve (V$_4$) and valve 5 (V$_5$) before measurement. The water vapor could never be introduced to the sample chamber before measurement. The passage of the vapor under measurement by switching V$_4$ and

V$_5$ is shown in Figure 3. The three-way tap (V$_5$) is turned through 180°, so as to connect the sample chamber with the hygrometer. Relative humidity (RH) of the humid mixed gas exhausted from the sample chamber was observed by the hygrometer (SECONIC ST-100SR; Takeda Rika Co., Tokyo, $\pm 1\%$ RH at 25°C). The measurable temperature range of this TG-DTA is from room temperature to 500°C. The higher limit of a sample weight is 500 mg and the lower limit of detection is 0.001 mg. The rate of water vapor (humidity) change in the TG-DTA chamber in which the PET film is placed is shown in Figure 5, which is drawn to demonstrate the relation of pressure (atm) and relative humidity ($p/p_0$) versus time. The accuracy of this method will be obvious from this graph.

## Measurement

The weight gain of PET film by sorption of water vapor was recorded at 1-s intervals by using the data collection system (microcomputer) of the TG-DTA. The weight of the sample film shows little change after the starting measurement because it takes some time for the water vapor to be supplied from valve 4 (V$_4$) to the sample film; however, it did not act as an obstacle to draw a sorption-rate curve since the vapor flow soon steadied out. Figure 6 definitively displays the sorption-rate curve. Apparent diffusion coefficients were determined in their gradients of initial slopes by
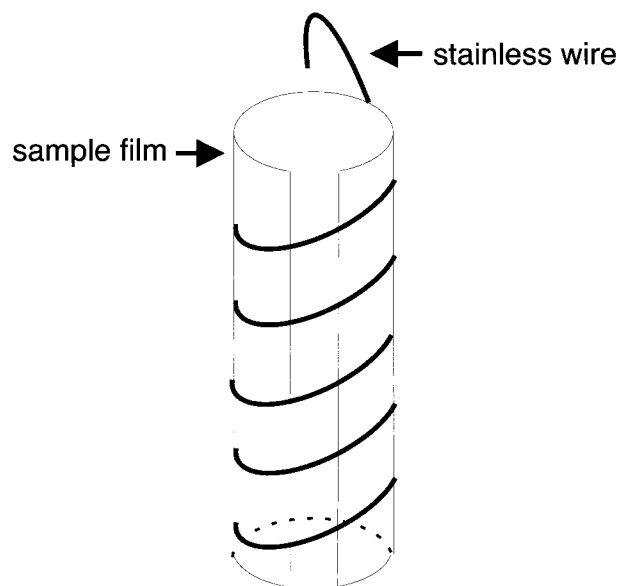


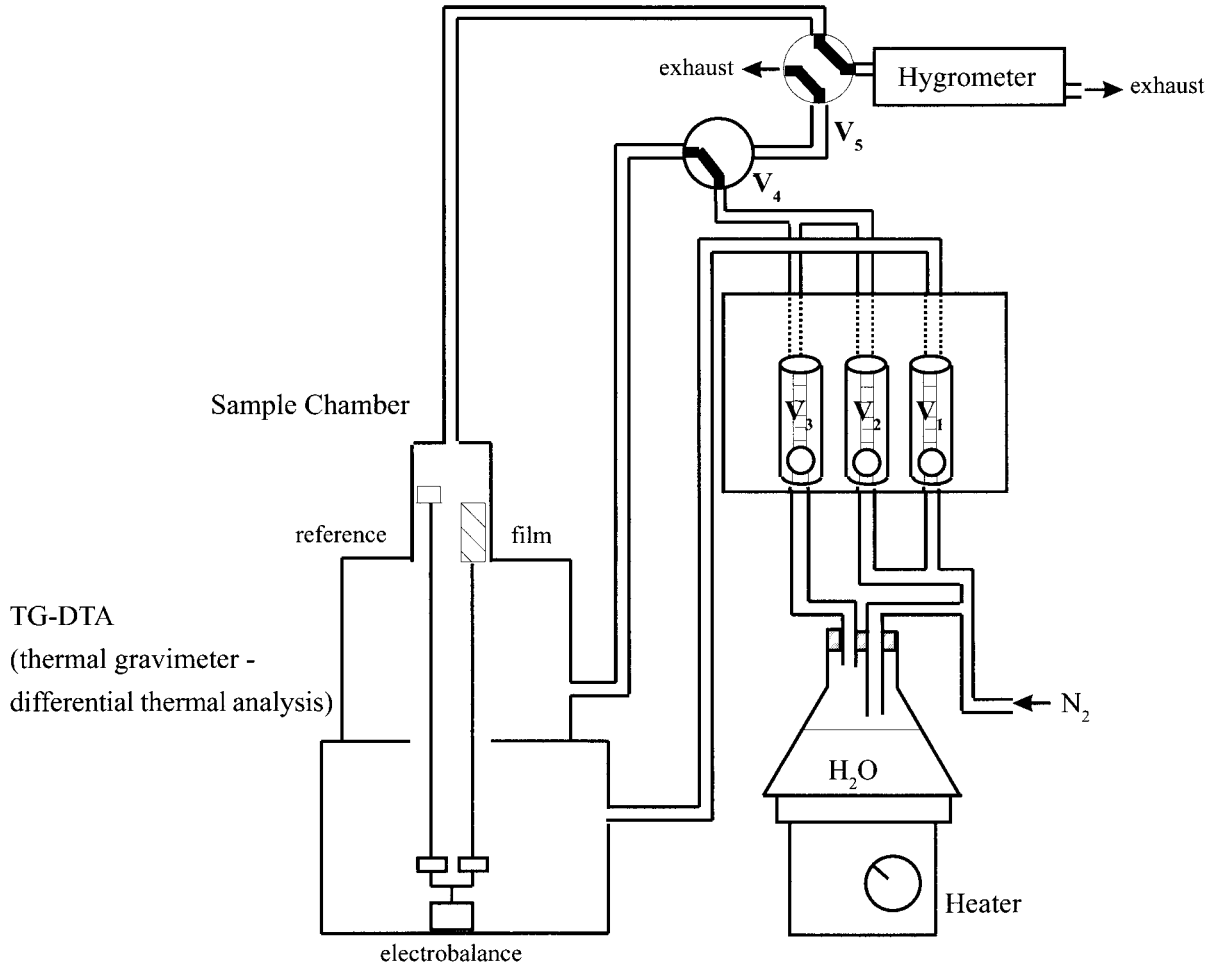**Figure 2** Mounting method of the sample film.

**Figure 3** Schematic diagram of water vapor sorption apparatus applying the TG-DTA.

the short-time method[3,4] and amounts of sorption were obtained from equilibrium sorption. Before the measurement, the sample was dried under about 60°C with dry nitrogen for about 7 h. The data were taken at 25, 35, and 45°C.

## RESULTS AND DISCUSSION

### Sorption-Rate Curve

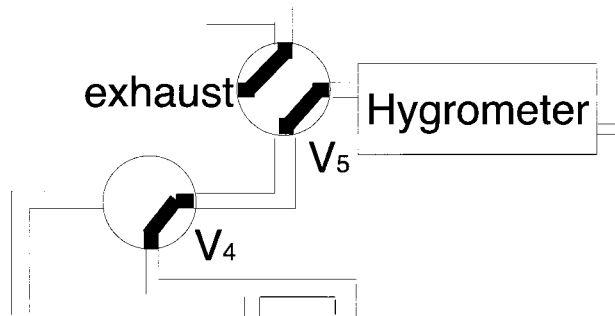The polymer film is well dried by dry nitrogen supplied from a pipe line. The film thickness is $l$.



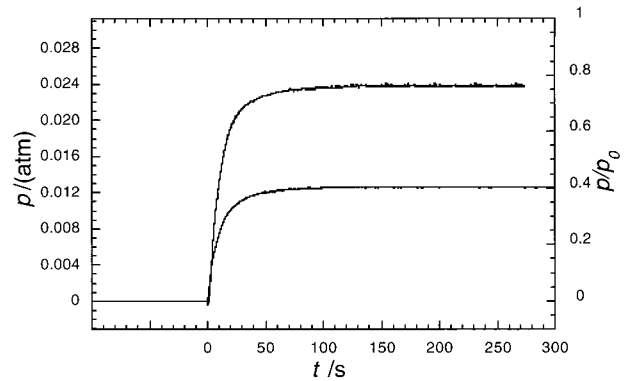**Figure 4** Positions of $V_4$ and $V_5$ in Figure 3 before measurement.



**Figure 5** The rate of water vapor pressure change in TG-DTA chamber at 25°C.

**Figure 6**  Sorption-rate curves for water vapor in PET film at 25°C. Points, observed values; solid lines, Fickian sorption equation.
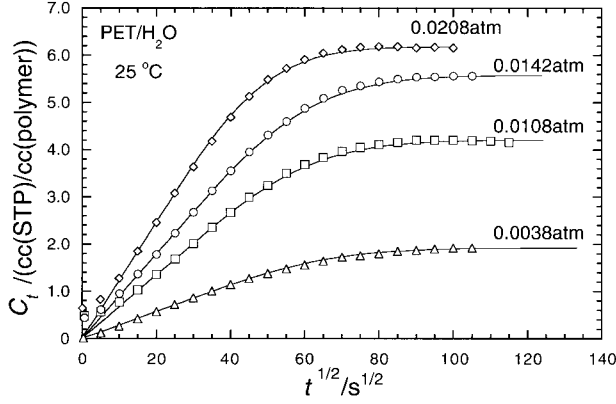


**Figure 7**  Sorption-rate curves for water vapor in PET film at 35°C. Points, observed values; solid lines, Fickian sorption equation.

The film is rapidly exposed to the water vapor at the pressure $p$. It is assumed that the water vapor sorption occurs simultaneously. It gives initial and boundary conditions as[5]

$$t = 0 \quad l/2 > x > -l/2 \quad C = 0$$
$$t \geq 0 \quad\quad x = 0 \quad\quad \partial C/\partial x = 0$$
$$t > 0 \quad\quad x = \pm l/2 \quad\quad C = k_D p$$

where $x$ is the coordinate in the direction of the film thickness and $C$ is the concentration of water vapor. The origin of the coordinate is fixed at the center of the film. Fick's second law is described as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{1}$$

where $D$ is the diffusion coefficient. On the basis of the preceding conditions, eq. (1) can be solved as a Fickian-type sorption rate equation[3,4]:

$$\frac{C_t}{C_e} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp\left[\dfrac{-D(2n+1)^2 \pi^2 t}{l^2}\right]}{(2n+1)^2}$$
$$\times \frac{(2n+1)\pi x}{l} \tag{2}$$

where $C_e$ is the amount of sorption at equilibrium of the sorption-rate curve from eq. (2) and $C_t$ is the amount at the time $t$. According to the short-time method, the apparent diffusion coefficient $D_e$ is calculated according to the following equation,
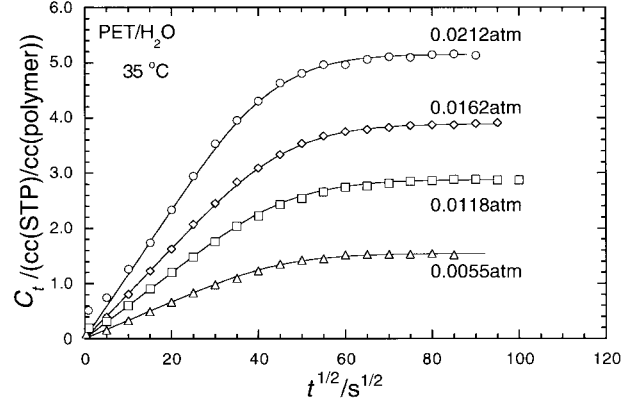
where $I_s$ is the gradient of the initial slope of the sorption rate curve:

$$D_e = \frac{\pi I_s^2}{16} \tag{3}$$

The experimental sorption-rate curves were compared with the calculated sorption-rate curves by use of the apparent diffusion coefficients $D_e$ and the equilibrium sorption $C_e$ determined from eq. (2) and experimental data. Figures 6, 7, and 8 show the sorption rate curves at 25, 35, and 45°C. Points represent experimental values and solid lines represent calculated curves.

Figures 6–8 suggest that water vapor sorption in PET is in accord with Fickian-type sorption. It is thought that clustering of water molecules and
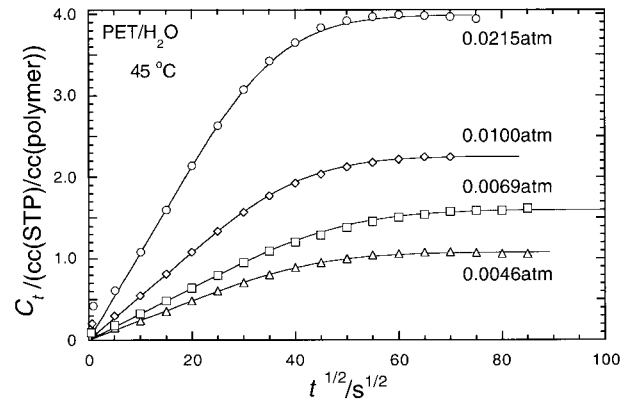


**Figure 8**  Sorption-rate curves for water vapor in PET film at 45°C. Points, observed values; solid lines, Fickian sorption equation.
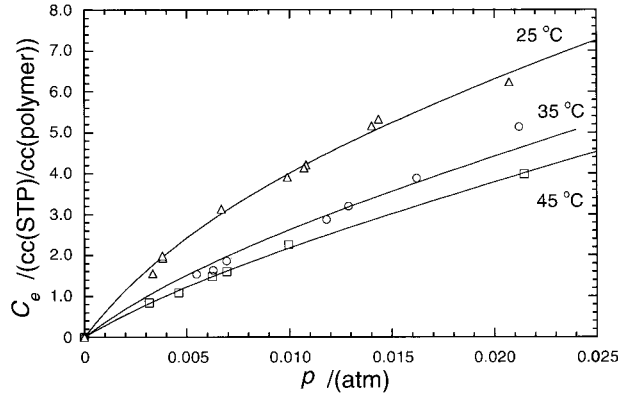
**Figure 9** Sorption isotherms for water vapor in PET film at 25, 35, and 45°C.

film relaxation by water vapor sorption in the range of the vapor pressure using this experiment did not occur. Because the amount of sorption of PET is small compared with the amount of sorption of other polymers, clustering did not occur even if vapor pressure increases. If clustering occurs, the marks in these figures did not agree with the solid lines according to Fickian-type sorption curves.

### Sorption Isotherms

If there is no interaction between penetrant and polymer, the concavity of the isotherms toward the pressure axis is observed at low pressure. As vapor pressure increases, the isotherms become linear. The dual-sorption model[6–12] is effective for analyzing such isotherms. The model is expressed as

$$C = C_D + C_H = k_D p + \frac{C'_H b p}{1 + bp} \qquad (4)$$

where

$k_D$ = Henry's low dissolution constant
$C'_H$ = hole saturation constant
$b$ = hole affinity constant
$p$ = pressure

Henry's law is obeyed by $C_D$ and Langmuir adsorption theory is obeyed by $C_H$. It is thought that the sorption system represented by $C_D$ is identical with dissolution of simple gas in organic liquid, that is, dissolution of penetrant into a polymer in proportion to gas-phase pressure. On the other hand, sorption by Langmuir adsorption theory is the adsorption of gas in microvoids or microcavity. In the case of this study, the sorption isotherms were depicted in the typical dual-sorption model, as shown in Figure 9. Table I shows the parameters of the dual-sorption parameters of the PET/water system with reference values of the PAN/water[13] and PET/CO$_2$[14] systems for comparison. The values of the parameters for the PET/water system are different from the PAN/water system, and because the amount of sorption for PET/water is small, the correlations of the values of three parameters agree between both systems. On the other hand, in comparison with the PET/CO$_2$ system, the amount of water vapor sorption is larger than the gas, and it is proven that line shapes of the sorption isotherms differ from each other. According to Figure 9, the sorption isotherms fit the dual-sorption equation; therefore, there are not clusters of water molecules in PET film at the vapor pressures used in this study. If clustering occurs, the sorption isotherms deviate from the straight lines and increase abruptly at high pressure. It is thought that to analyze the isotherms of water vapor sorption in PET film, the dual-mode sorption model is more effective than the BET equation[15,16] and the extended dual-mode sorption model.[13]

**Table I   Dual-Sorption Parameters of Water in PET, Water in PAN, and CO$_2$ in PET Systems**

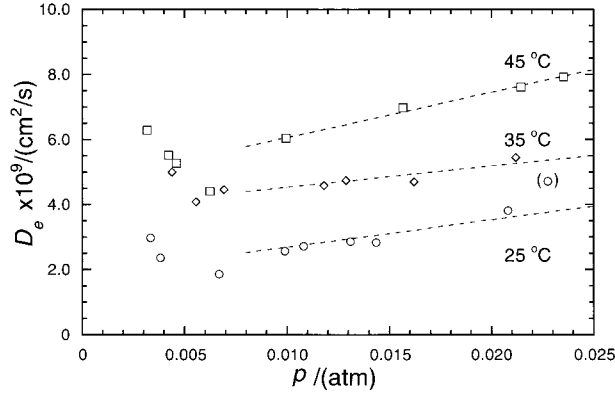| System Type | $T(°C)$ | $k_D \left( \dfrac{\text{cc(STP)}}{\text{cc(polymer)}} \text{atm}^{-1} \right)$ | $C'_H \left( \dfrac{\text{cc(STP)}}{\text{cc(polymer)}} \right)$ | $b(\text{atm}^{-1})$ |
|---|---|---|---|---|
| PET/H$_2$O | 25 | 140.864 | 5.291 | 96.278 |
| | 35 | 136.450 | 2.581 | 94.624 |
| | 45 | 130.326 | 1.838 | 90.285 |
| PAN/H$_2$O | 45 | 243 | 1.44 | 40 |
| PET/CO$_2$ | 45 | 0.260 | 4.96 | 0.282 |

**Figure 10** The apparent diffusion coefficients for water vapor in PET film at 25, 35, and 45°C. Points, observed values; dashed lines, regressions of observed values.
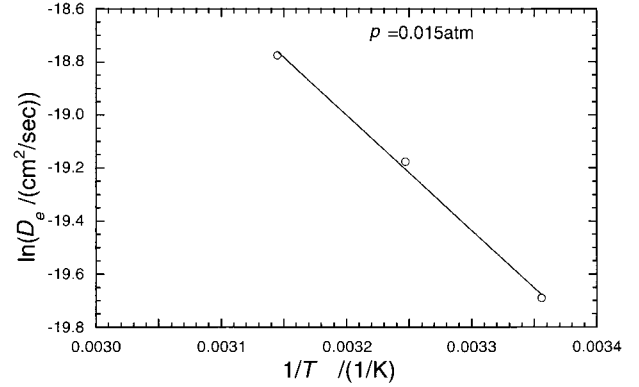


**Figure 11** Diffusion coefficient versus reciprocal of absolute temperature for water vapor in PET film. Points, observed values; solid line, linear regressions of observed values.

## Diffusion Coefficients

The apparent diffusion coefficient was determined according to eq. (3) from Figure 5, where $I_s$ is the gradient of the initial slope of the sorption rate curve , as mentioned earlier.

$$D_e = \frac{\pi I_s^2}{16} \qquad (3)$$

In this study, the apparent diffusion coefficients had to be determined using the more troublesome method, because it takes some time to reach an equilibrium humidity in TG-DTA from opening valve 4. We then used the data of $C_t/C_e$ in the range of 0.3–0.5 to calculate the slope $I_s$ of eq. (5):

$$\frac{C_t}{C_e} = \frac{I_s}{l} t^{1/2} \qquad (5)$$

where $C_t$ is the amount of water in the film at time $t$ and $C_e$ is the total amount of water in the film at the infinite time. The apparent diffusion coefficient $D_e$ is calculated from $I_s$ and eq. (3).

Figure 10 shows the pressure dependency of the apparent diffusion coefficients for the PET/water system. The apparent diffusion coefficient increased with vapor pressure. In this case, different diffusion coefficients were assigned to the water vapor sorbed by each of the two mechanisms and obtained the following expression for the flux $N$ as the partial immobilization model[17–23] developed by Paul and Koros:

$$N = -D_D \frac{\partial C_D}{\partial x} - D_H \frac{\partial C_H}{\partial x} \qquad (6)$$

where $D_D$ is the diffusion coefficient of the Henry part and $D_H$ is the diffusion coefficient of the Langmuir part. Our results for the PET/water system have been interpreted in terms of a concentration-dependent diffusion coefficient, which is shown to be mathematically equivalent to the partial immobilization model. Consequently, it turned out that diffusion of water vapor in PET was in accord with the partial immobilization model.

Our future analysis with these results should help to arrive at a proper description of water vapor sorption and diffusion in PET or in the glassy polymers.
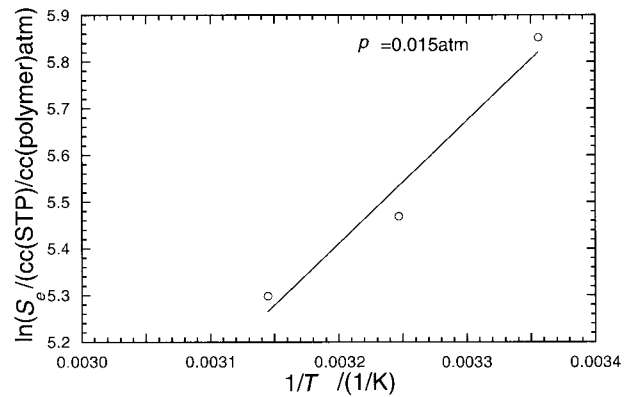


**Figure 12** Solubility coefficient versus reciprocal of absolute temperature for water vapor in PET film. Points, observed values; solid line, linear regressions of observed values.

**Table II   Temperature Dependencies of Diffusion Coefficient and Dual-Sorption Parameters for Water in PET, Water in PAN, and CO$_2$ in PET Systems**

| System Type | $E_D$/(kJ/mol) ($p = 0.015$ atm) | $\Delta H_S$/(kJ/mol) ($p = 0.015$ atm) | $\Delta H_D$/(kJ/mol) | $\Delta H_b$/(kJ/mol) |
|---|---|---|---|---|
| PET/H$_2$O | 36.10 | $-21.90$ | $-3.06$ | $-2.52$ |
| PAN/H$_2$O | — | — | $-40.3$ | $-71.8$ |
| PET/CO$_2$ | — | — | $-7.14$ | $-12.6$ |

## Temperature Dependencies

### Diffusion Coefficient

The temperature dependency of the apparent diffusion coefficients $D_e$ of the PET/water system at pressure 0.015 atm is displayed in Figure 11. The activation energy for diffusion $E_D$ is obtained by the Arrhenius equation,[24–26]

$$D_e = D_0 \exp\left(-\frac{E_D}{RT}\right) \tag{7}$$

Equation (7) reflects the mechanism of diffusion as follows. In this case, $E_D$ is the constant since plotting ln $D$ versus $1/T$ is linear. If the interactions between the polymer segments are stronger, the larger activation energy for diffusion is needed to form the microvoids.

### The Solubility Coefficient

The temperature dependency of apparent solubility coefficients $S_e$ of the PET/water system at pressure 0.015 atm (as shown in Figure 12) is represented by van't Hoff's law,

$$S_e = S_0 \exp\left(-\frac{\Delta H_S}{RT}\right) \tag{8}$$

where $\Delta H_S$ is the heat of sorption.

The values of both $E_D$ and $\Delta H_S$ are shown in Table II with the temperature dependencies of the dual-sorption parameters.

### Parameters of Dual-Mode Sorption

The temperature dependencies of the Henry's law constant $k_D$ and the hole affinity constant $b$ are represented the same as the solubility coefficient[10,27]:

$$k_D = k_{D_0} \exp\left(-\frac{\Delta H_D}{RT}\right) \tag{9}$$

$$b = b_0 \exp\left(-\frac{\Delta H_b}{RT}\right) \tag{10}$$

where $\Delta H_D$ is the heat of dissolution in Henry's law limit and $\Delta H_b$ is the heat of sorption in the Langmuir mode. Semilog plots of the parameters
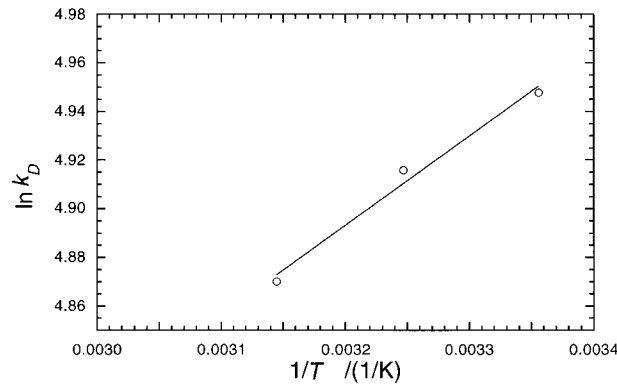


**Figure 13**   Henry's law constant versus reciprocal of absolute temperature for water vapor in PET film. Points, observed values; solid line, linear regressions of observed values.



**Figure 14**   Hole affinity constant versus reciprocal of absolute temperature for water vapor in PET film. Points, observed values; solid line, linear regressions of observed values.
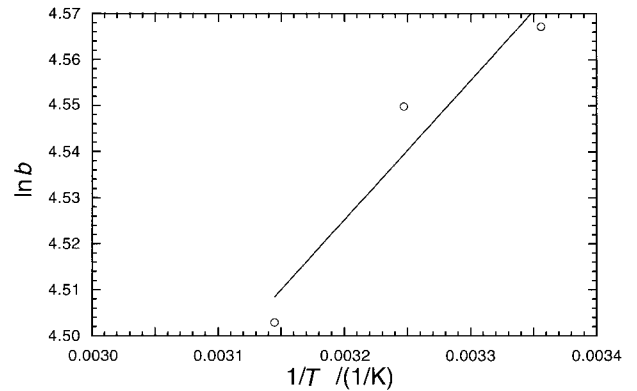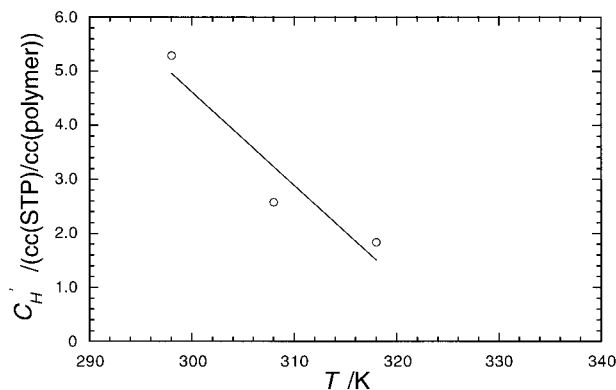
**Figure 15**  Hole saturation constant versus absolute temperature for water vapor in PET film. Points, observed values; solid line, linear regressions of observed values.

$k_D$ and $b$ versus $1/T$ are shown in Figures 13 and 14, respectively. The values of $\Delta H_D$ and $\Delta H_b$ were determined from the least-square fits of eqs. (9) and (10), respectively. It is seen that $k_D$ and $b$ decrease with increasing temperature, as has been observed for a number of light penetrant gases in many glassy polymers. The values of $\Delta H_D$ and $\Delta H_b$ are presented in Table II.

On the other hand, the tendency of the $C'_H$ data decreases with increasing temperature, as shown in Figure 15. Data from many studies demonstrated that the measured values of $C'_H$ for the glassy polymer/$CO_2$ system were extrapolated to zero at temperatures near the experimentally determined glass-transition temperatures of the respective polymers. In the case of the PET/water system, this tendency is ambiguous.

## CONCLUSIONS

PET is a polymer with very small water vapor sorption. It was proven that the amount of the sorption to the polymer with such a small quantity of water vapor sorption could be measured using TG-DTA. Although this equipment successfully measures the sorption quantity of small quantities of water vapor, the equipment can introduce inaccuracies of measurement by the condensation of the water vapor. For this reason, further investigation is necessary in high-temperature environments and at high-pressure measurements. From the sorption-rate curve, it was proven that the sorption-rate curve of water vapor for PET was the Fickian type. In PET, clusters of water molecules were not found from the sorption isotherms, because the measured iso-

therms were reproduced by the dual-sorption model and the dual-sorption parameters.

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