

# Diffusion and Sorption for Carbon Dioxide in Kapton at Extremely Low Pressure

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**ABSTRACT:** Pressure-dependent solubility and diffusion coefficients for carbon dioxide in glassy polymers have been well described using the "dual sorption and transport model." However, the plastization effect by high-pressure carbon dioxide seems to promote the pressure dependence of the sorption and transport coefficients. To avoid the relaxation process by the plastization which is superimposed on the diffusion process, the diffusion and sorption of carbon dioxide were measured at extremely low pressure (below 1 cmHg). Linear isotherms observed for CO<sub>2</sub> sorption into Kapton were interpreted in terms of the dual model equation at extremely low pressure. From the permeation curve of the Kapton/CO<sub>2</sub> system, the diffusion and permeation coefficients were obtained according to the usual manner, and both coefficients were independent of pressure. Sorption and transport parameters were obtained from sorption isotherms and average values of the permeation coefficients. The parameters thus obtained were substituted in an approximated dual sorption and transport equations at extremely low pressure and the pressure independence of the diffusion and permeation coefficients were sufficiently reproduced. It is a good technique to experiment at such extremely low pressure when the validity of the dual model is evaluated. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1013–1017, 1998

**Key words:** diffusion and sorption; Kapton/carbon dioxide system; extremely low pressure; dual sorption and transport parameters

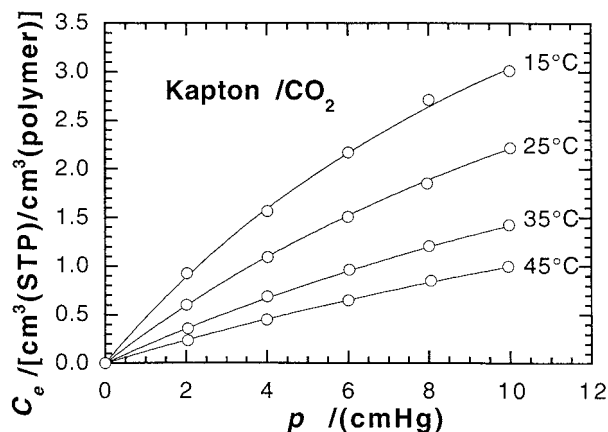
## INTRODUCTION

When the sorption experiment is carried out via changing the gas pressure into glassy polymers, the relation between the equilibrium sorption amount and pressure obeys so-called dual sorption model, and the dual sorption parameters are calculated from the experimental values and the model equation. Also, then, the measurement val-

ues are reproduced from the dual sorption parameters and the model equation. Similarly, the dual transport model equation can be applied to the apparent permeation coefficient from the permeation experiment. The dual transport parameters can be obtained by the conventional method and the pressure dependence of the permeation coefficient can be reproduced by the dual transport parameters and the dual transport model equation. To discuss the validity of these models, the pressure dependence of the diffusion coefficient obtained from an analytical method by using these parameters should reproduce the diffusion

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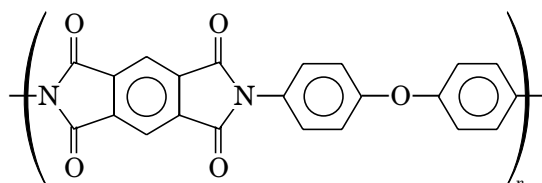


**Figure 1** Sorption isotherms for CO<sub>2</sub> in Kapton film at various temperatures from the sorption experiment. The points are observed values. Solid lines are calculated by the dual sorption model equation.

coefficient from experiment. However, thus far, such an examination has not been attempted. In these cases, when the high-pressure gas interacts with the polymer, the relaxation phenomenon by plasticity occurs, and a pressure-dependence phenomenon should be superimposed. Then, it is necessary to distinguish this phenomenon from the dual models. In this study, using Kapton, which is a typical polyimide, below 10 cmHg of CO<sub>2</sub> where the plasticity is not able to occur easily, the validity of the dual model is discussed for the apparent diffusion coefficients which were obtained from the sorption and permeation experiments.

## EXPERIMENTAL

The Kapton polyimide membrane [glass transition temperature ( $T_g$ ), 350–450°C] used in this study is a glassy amorphous polymer membrane with exceptional chemical and thermal stability, which was provided by the Mitsubishi Kagaku Corp (Yokohama, Japan):



Kapton polyimide

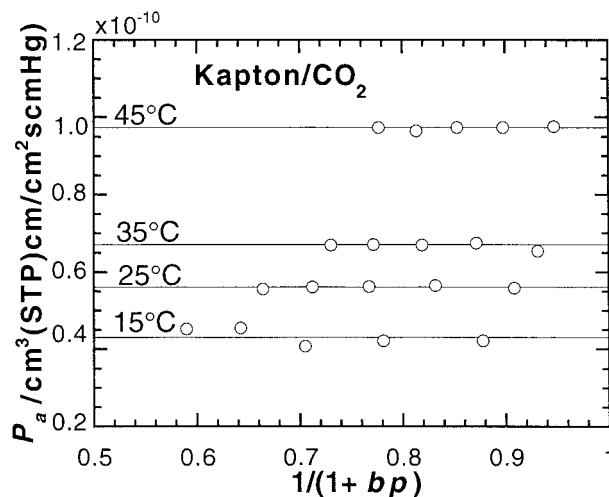
The membrane density is 1.4652 obtained from

a density gradient column using a carbon tetrachloride/*n*-heptane mixture at 25°C. DSC studies using a Rigaku differential scanning calorimeter failed to show a prominent glass transition temperature near 350–450°C. The membrane thickness was determined by weighing a membrane of a known area and was found to be  $26.06 \times 10^{-4}$  cm (area: 96.97 cm<sup>2</sup>) for the sorption experiment and  $25.10 \times 10^{-4}$  cm (area: 4.524 cm<sup>2</sup>) for the permeation experiment.

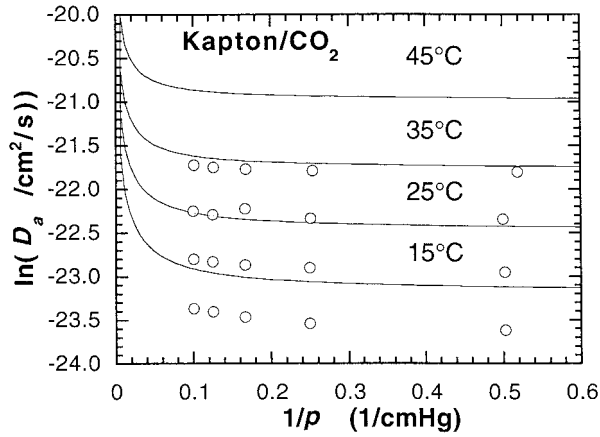
The apparatus and procedure for gas-sorption experiments have been described elsewhere.<sup>1,2</sup> In this case, pressure is very low. To keep the same level of gain from a digital multimeter, the volume of the sample was increased about 10 times in the case of the conventional pressure experiment. The equilibrium sorption amount ( $C_e$ ) was obtained from the sorption-rate curve. The apparatus for gas permeation was the same as described elsewhere.<sup>3</sup> The apparent diffusion coefficient ( $D_a$ ) and the apparent permeation coefficient ( $P_a$ ) were calculated by the time-lag method and from the linear slope of the permeation-rate curve.<sup>4</sup>

## RESULTS AND DISCUSSION

The sorption isotherms for carbon dioxide at low pressure below 10 cmHg and at various temperatures are described well by the dual sorption model<sup>5–7</sup>:



**Figure 2** Pressure dependence of the apparent permeation coefficients for CO<sub>2</sub> in Kapton film at 2–10 cmHg pressure and at 15–45°C temperature. The points are observed values. Solid lines are averages.



**Figure 3** Pressure dependence of the apparent diffusion coefficients from the permeation experiment for CO<sub>2</sub> in Kapton film at 2–10 cmHg pressure and at 15–45°C temperature. The points are observed values. Solid lines are calculated by eq. (4).

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

where  $b$ ,  $C'_H$ , and  $k_D$  are dual sorption parameters. The sorption data were analyzed according to eq. (1) using a nonlinear least-squares regression. The dual sorption parameters were determined in the conventional manner.<sup>8</sup> Using these parameters and eq. (1), the observed data were fitted by calculated solid lines, as shown in Figure 1.

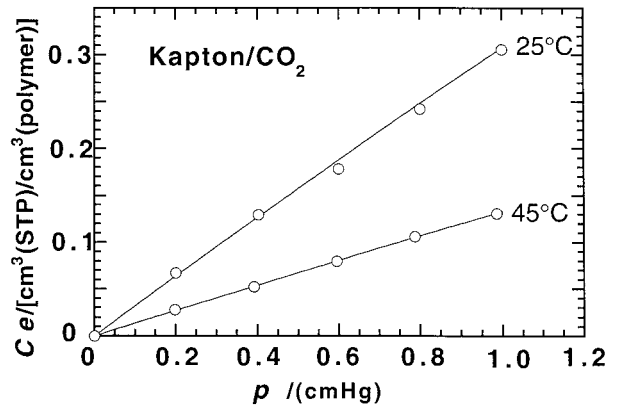
The dual transport parameters can be deduced from the dual sorption parameters and the pressure dependence of the permeation coefficients, using eq. (2)<sup>9</sup>:

$$P_{a(\text{cal})} = \frac{k_D D}{76} \left( 1 + \frac{FK}{1 + b p} \right) \quad (2)$$

where  $K = b C'_H / k_D$ , and  $F$  and  $D$  are dual transport parameters. When the relations of the apparent permeation coefficients ( $P_a$ ) versus  $1/(1 + b p)$

**Table I Dual Sorption and Transport Parameters Determined from Sorption and Permeation Experiments (2–10 cmHg)**

Temperature	$b$	$C'_H$	$k_D$	$D \times 10^9$	$F$
15°C	5.31	6.99	1.27	2.06	0
25°C	3.85	6.11	1.01	3.39	0
35°C	2.81	4.85	0.87	4.64	0
45°C	2.20	4.05	0.67	6.48	0

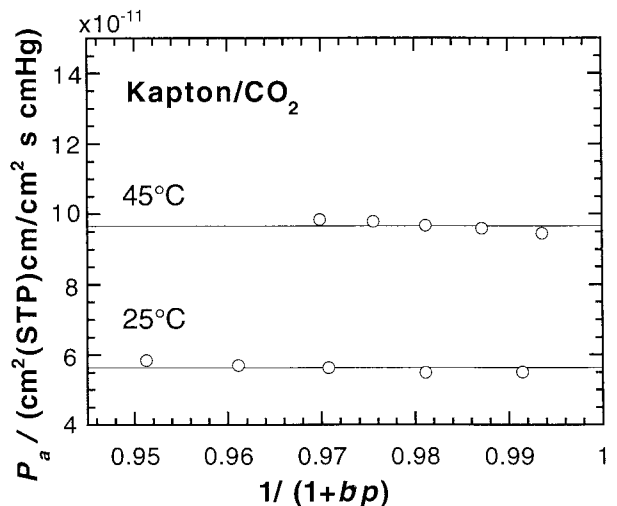


**Figure 4** Sorption isotherms for CO<sub>2</sub> in Kapton film at 0.2–1.0 cmHg pressure and at 25 and 45°C temperature from the sorption experiment. Symbols as in Figure 1.

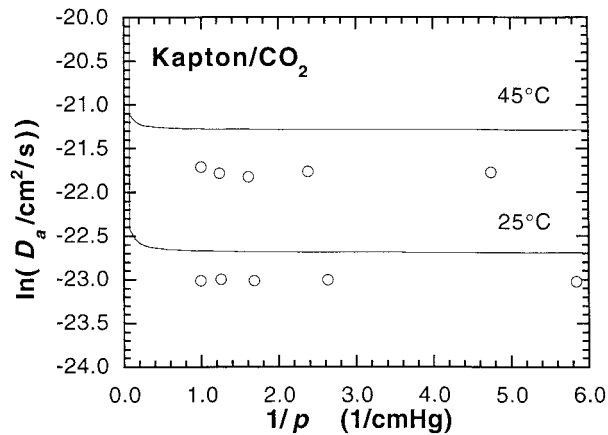
were plotted at the same pressure and temperature ranges as the sorption experiment, the curves did not show any pressure dependence, as shown in Figure 2, meaning that  $F$  becomes 0 in eq. (2). Then, this model equation can be approximated like eq. (3):

$$P_{a(\text{cal})} = \frac{k_D}{76} D \quad (3)$$

Also, the diffusion coefficient ( $D$ ), which is also the dual transport parameter, is determined from the average value of  $P_a$  and  $k_D$  obtained from the



**Figure 5** Pressure dependence of the apparent permeation coefficients for CO<sub>2</sub> in Kapton film at 0.2–1.0 cmHg pressure and at 25 and 45°C temperature. Symbols as in Figure 2.



**Figure 6** Pressure dependence of the apparent diffusion coefficients for CO<sub>2</sub> in Kapton film at 0.2–1.0 cmHg pressure and at 25 and 45°C temperature. Symbols as in Figure 3.

sorption experiment. The measurement values could be reproduced by drawing the solid line from the dual transport parameters and the model eq. (3), as shown in Figure 2.

The apparent diffusion coefficients determined from the permeation experiment at similarly low pressure and each temperature were plotted by the reciprocal of the pressure, as shown in Figure 3. The pressure-dependence equation of  $D_a$  was solved analytically by Paul et al.,<sup>10</sup> and it can be approximated by  $F = 0$  as eq. (4):

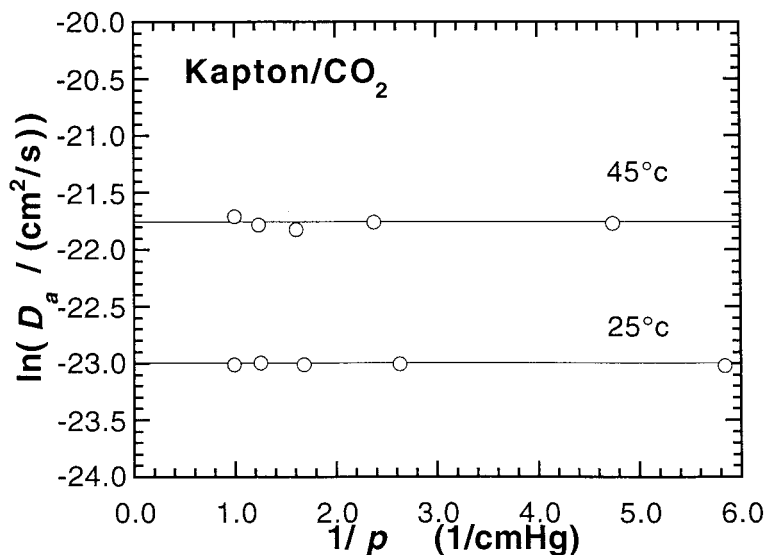
$$D_{a(\text{cal})} = \frac{D\{1 + FK/(1 + bp)\}^3}{1 + Kf(bp)} \Rightarrow \frac{D}{1 + Kf(bp)} \quad (4)$$

However, the solid lines which were drawn by substituting the dual sorption and transport parameters into eq. (4) could not reproduce the experimental values. The dual sorption parameters  $k_D$ ,  $C'_H$ , and  $b$  and the dual transport parameters  $D$  and  $F$  for Kapton/CO<sub>2</sub> at 15–45°C, used above, are listed in Table I. From the results up to here, it becomes impossible to reproduce the pressure dependence for the diffusion coefficient even within this range of pressure by the same parameter as the amount of the equilibrium sorption and other transport coefficients.

The experiment was continued for extremely low pressures. The sorption isotherm curves of 25 and 45°C became straight lines for the pressure range which was reduced by one order, at pressure 0.2–1.0 cmHg, as shown in Figure 4, that is,  $bp$  becomes considerably small compared with 1 ( $bp \ll 1$ ), and the model equation can be approximated like eq. (5):

$$C_e = k_D p + \frac{C'_H b p}{1 + b p} \Rightarrow (k_D + C'_H b)p (bp \approx 0) \quad (5)$$

Using eq. (5), the experimental values could be reproduced by the same parameters at the range of pressure which was 10 times higher and which had been worked out before (Table I).



**Figure 7** Pressure dependence of the apparent diffusion coefficients for CO<sub>2</sub> in Kapton film at 0.2–1.0 cmHg pressure and at 25 and 45°C temperature. The points are observed values. Solid lines are averages.

**Table II Dual Sorption and Transport Parameters Determined from Sorption and Permeation Experiments (0.2–1.0 cmHg)**

Temperature	$b$	$C'_H$	$k_D$	$D \times 10^9$	$F$	$f(bp)$
25°C	3.85	6.11	1.01	3.46	0	1.38
45°C	2.20	4.05	0.67	11.04	0	1.66

Next, the apparent permeation coefficients  $P_a$  obtained from this extremely low pressure at 25 and 45°C were plotted versus  $1/(1 + bp)$ . The pressure dependencies were not found, the same as in the experiment at 2–10 cmHg, as shown in Figure 5. The dual transport parameters  $D$  and  $F$  were determined from the average value of  $P_a$  obtained from the extremely low-pressure experiment, and  $k_D$ , obtained from the experiment at pressure 2–10 cmHg. In addition, the apparent diffusion coefficient was plotted against the reciprocal of the pressure, as shown in Figure 6. It is not possible to reproduce the pressure dependence of the apparent diffusion coefficient by the dual transport equation [eq. (4)], although the observed diffusion coefficient no longer depends on the pressure, meaning that  $F$  becomes 0 and  $f(bp)$  becomes a constant. The model equation [eq. (4)] of the pressure dependence for the diffusion coefficient becomes an equation by which the straight line is shown. Then, when  $D$  and  $f(bp)$  were determined using the dual sorption parameter, the measurement value of  $D_a$  could be reproduced from the model equation, as shown in Figure 7. The pressure dependencies for the equilibrium sorption amount  $C_e$  and two transport coefficients  $P_a$  and  $D_a$  were able to be reproduced in the range of 0.2–1.0 cmHg pressures by the use of the same dual sorption and transport parameters. These parameters are listed in Table II.

From the above-mentioned results, it can be said that the pressure dependence for the equilibrium sorption amount ( $C_e$ ) obtained by the experiment is found to be linear and the approximation used as  $bp \rightarrow 0$  is valid if the measurement is carried out at the extremely low pressures below 1 cmHg. By reducing the pressure and assuming that  $f(bp) = \text{constant}$ , it is possible to reproduce the equilibrium sorption amount and two transport coefficients which could not be reproduced above 1 cmHg by the same parameters. Therefore, to discuss the validity of the dual sorption and the transport model, it has been understood that the experiment by such low pressure is preferable. Although the measurement values are in fair agreement with the model values when assuming  $f(bp) = \text{constant}$ , it will be necessary to examine the meaning of these constant values.

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