Permeation of Gases and a Gas Mixture through a Polymer Membrane in the Glass Transition Region

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Permeation behavior of carbon dioxide, acetone vapor, and their mixture through poly(vinyl acetate) membrane was studied at 30°C in the pressure region below 1 atm. The temperature of experiments is in the vicinity, slightly above, the glass transition temperature of the system concerned. Total pressure of the gas mixture was 1 atm. The permeability coefficient P for pure carbon dioxide was independent of pressure, while P for carbon dioxide in permeation of the gas mixture increased with increasing partial pressure of acetone. On the other hand, P for pure acetone increased with increasing pressure, and no effect of the partner gas was observed in permeation of the gas mixture. The behavior is in agreement with that predicted by the free-volume model, but not with that of the dual-mode transport model. At low partial pressures of acetone, the free-volume model predicts well value of P for carbon dioxide in the mixed-gas permeation. In the region of higher partial pressure of acetone, however, the deviation of measured values of P from the predicted dependence of P on partial pressure of acetone was observed. This suggests that the permeation behavior of the gas mixture in the glass transition region is not fully controlled by the free volume content of the system.

INTRODUCTION

The permeation behavior of mixtures of gases and vapors through nonporous polymer membranes has attracted much attention in recent years. Although many studies have been made on this subject, still a little information is available on fundamental characteristics of permeation behavior of the gas mixtures in comparison with that of pure gases or vapors.[1-8] If component gases exhibit very low solubilities in polymer, each gas molecule permeates independently through the polymer membrane, and permeation characteristics of the gas mixture are predicted from permeation data of pure gases.[1,2,5] In the case of permeation of mixtures of more soluble gases, however, permeation of a component gas affects much that of other components, and permeation behavior of the gas mixture is not simply correlated with that of pure component gases.

According to the state of penetrant-polymer systems, the permeation behavior of gas mixtures has been explained in terms of different models, the dual-mode transport, or mobility, model and the free-volume model, though both models stem from the solution-diffusion concept for permeation proposed by Graham many years ago.[9] If a

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system concerned is in the glassy state, the dual-mode transport model is employed to interpret permeation behavior of gas mixtures. On the other hand, permeation behavior of a system of gas mixture and rubbery polymer is analyzed in terms of the free-volume model. One can find many articles in the literature, which show these models respectively explain well the permeation behavior observed in the glassy and the rubbery regimes, both are far from the glass transition of a given system.[1,4-8] However, concerning the permeation behavior of gas mixtures in the glass transition region, a model which can be used to analyze the behavior observed in this region has not yet been developed. Also, as far as the authors' knowledge, no attempt has been made experimentally in order to elucidate the permeation characteristics of a penetrant-polymer system in the glass transition region.

This paper describes permeation behavior of carbon dioxide, acetone vapor, and their mixtures through poly(vinyl acetate) (PVAc) membrane. The objective of the present study is to clarify caracteristic features of permeation of gas mixture through polymer membrane in the glass transition region. The glass transition temperature of PVAc is reported as 28–31°C,[10] and permeation measurements were made at 30°C. Carbon dioxide and acetone vapor were selected as penetrants because of their relatively high permeability in PVAc.

BACKGROUND

The Dual-Mode Transport Model

This model has been formulated based upon the dual-mode sorption model.[5-8] For systems of a gas and a glassy polymer, sorption isotherms are frequently concave to the pressure axis, approaching linearity at higher pressures. The sorption isotherm of this shape has been described by assuming that the penetrant dissolves by two component processes : ordinary dissolution in a continuous amorphous matrix, the concentration of this mode C_D is represented by Henry's law, and sorption in micro-voids or holes, the concentration C_H is represented by the Langmuir equation. The total concentration C of sorbed penetrant is then given by the expression of the dual-mode sorption model:

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

where k_D is the Henry's law constant, p is pressure, and C_H' and b are respectively the Langmuir constant and affinity constant.

By assuming that the penetrant species dissolved in microvoids is partially mobilized, the pressure dependence of permeability coefficient P is expressed as

$$P = k_D D_D[1 + FK/(1+bp)] \tag{2}$$

where $F = D_H/D_D$, $K = C_H' b/k_D$, and D_D and D_H are diffusion coefficients characterizing the mobility of the penetrant in the two sorption modes. The dual-mode transport model predicts that P decreases with increasing penetrant pressure.

For cases involving only weak penetrant-penetrant and penetrant-polymer interactions, Koros et al. have shown that the dual-mode transport model can provide a

description of the transport of gas mixture in glassy polymers.[22] They give the following expression for the permeability coefficint for component A in a binary-component feed when the downsteam pressure can be approximated as zero:

$$P_A = k_D D_{DA} [1 + F_A K_A/(1 + b_A p_A + b_B p_B)] \qquad (3)$$

Compared with Eq. (2), an additional term appearing in the denominator of the second term of Eq. (3) reflects the competition of the mixture for the limited microvoid capacity in the glassy polymer.[11,12] The permeability coefficient of either component is, therefore, predicted to be decreased due to the presence of the other component which competes with it for sorption and transport pathways in the membrane. The predicted depression of the permeability coefficient for one component by the other have been substantiated in permeation behavior of several systems of a binary gas mixture and a polymer in the glassy state.[7]

The Free-Volume Model

The free-volume model, which was developed by Fang et al. to represent permeation data of gas mixtures through rubbery polymers,[13] is based on an earlier model proposed by Fujita.[14] The validity of Fujita's model has been demonstrated for a number of systems of organic vapor and amorphous polymer in the rubbery state, which exhibit a strong dependence of the diffusion coefficient on penetrant concentration.[1,4,6,8]

Fang et al. extended Fujita's free-volume model to the permeation of gas mixtures through rubbery polymers by assuming that the effect of the components of a mixture on the free volume of the penetrant-polymer system is additive. This assumption appears reasonable for systems with total penetrant concentrations of less than about 0.2 volume fraction. If the penetrant molecules do not differ much in size and shape, the permeability coefficient for component A of a binary mixture is given by the following relation when the downstream pressure is negligibly smaller than the up-stream one:

$$\ln P_A = C_A(T) + m_A(T) p_A + (B_{dA}/B_{dB}) m_B(T) p_B \qquad (4)$$

where $C_A(T)$, $m_A(T)$, B_{dA}, B_{dB} are parameters. The parameters $C_A(T)$ and $m_A(T)$ can be determined fom permeability measurements with pure A, and the ratio B_{dA}/B_{dB} can be estimated approximately from the relation $B_{dA}/B_{dB} = (d_A/d_B)^2$ where d is the molecular diameter of the penetrant. Eq. (4) predicts that P in permeation of a pure component increases with increasing pressure and that P_A in permeation of a binary gas mixture is greater than that of pure gas permeation. Thus, the free-volume model predicts opposite pressure dependence of the permeability coefficient to that predicted by the dual-mode transport model. Eq. (4) described satisfactorily the permeation of gas mixtures through polyethylene[15] and rubbery phase of styrene-butadiene block copolymer[16] membranes.

EXPERIMENTAL

Materials

A purified sample of poly(vinyl acetate) (PVAc) was generously provided by Mr. T. Okaya of Kuraray Co., Ltd. The viscosity-average degree of polymerization of the sample quoted by the supplier was 1,750. Films used for measurements were prepared by the solvent-casting method. Acetone of G. R. grade was used as casting solvent. A polymer solution of about 5% was poured onto a clean mercury surface, and the solvent was allowed to evaporate slowly in a desiccator at room temperature. After having dried two days in vacuum at room temperature, the films were leached in distilled water for four days in order to remove final traces of acetone, and dried again in vacuum at room temperature. Finally, the films obtained were annealed at 50°C for an appropriate interval of time. The film thickness was determined by taking the arithmetic average of numerous readings of a micrometer screw gauge over the area of the film. Measurements of the film thickness were made at a temperature below 25°C. The glass transition temperature T_g was measured employing a DSC thermal analyzer (Rigaku Denki, Model 8000) by heating from 200 to 330 K at the rates of 10, 5, 2.5, and 1.25 K min^{-1}. The value of T_g was estimated to be 28°C by taking into account of the heating rates.

Carbon dioxide and acetone were used as penetrants. The purity of carbon dioxide gas quoted by the supplier exceeded 99.9% by volume. Acetone was of G. R. grade, and no attempt was made to effect further purification.

Methods

Permeation measurements were made by a permeation apparatus for mixed gases and vapors.[16] The apparatus utilizes the carrier gas method with gas-chromatographic analysis to determine the individual cahracteristics of component gases. To measure the permeation behavior of pure acetone vapor, the carrier gas helium saturated by acetone vapor was supplied to the upstream side of the polymer membrane. The vapor/gas mixture was obtained by bubbling helium through acetone in a liquid reservoir which was immersed in a water bath regulated to ±0.05°C. In order to effect the saturation procedure, glass beads of 5 mm diameter were filled in a lower half of the reservoir. Pressure of acetone vapor was varied by changing the temperature of the liquid reservoir. By replacing helium to carbon dioxide, mixtures of carbon dioxide and acetone vapor were obtained.

In measurements with gas samples contained acetone vapor, a modification of the permeation cell unit of the permeation apparatus[16] was made because of high permeability of acetone. The carrier gas flow was introduced to a stainless-steal tubing which connects the downstream side of the permeation cell to a gas chromatograph. The sampling loop is in the tubing, and a port of the tubing was open to the atmosphere. At every given time interval, the permeating mixture in the sampling loop was introduced to the gas chromatograph by the carrier gas stream. This modification is to avoid unfavorable increase of partial pressure of highly permeable component in the downstream side of the permeation cell. The total pressure of gas mixtures was

fixed at 1 atm. Permeation measurements with pure carbon dioxide were performed by the cell partition method. Details of the apparatus and procedure have been described elsewhere.[17] The permeability coefficient was calculated from the permeation rate at steady state.

The sorption experiments were carried out using a sorption apparatus equipped with an electromagnetic microbalance (Chyo Balance Corp., Model GAB-1). Carbon dioxide was introduced from a gas cylinder via a reduction valve to a gas reservoir of the apparatus. Acetone was degassed in a liquid reservoir by successive freezing, pumping, and thawings, and then the vapor was introduced in the gas reservoir.

All measurements were made at 30°C. This temperature is slightly above the glass transition temperature of the system concerned.

RESULTS AND DISCUSSION

Sorption Isotherms

Figure 1 shows the sorption isotherms of carbon dioxide and acetone in PVAc at 30°C. Here, the ordinate, C, represents the amount of penetrant in cm³ at the standard temperature and pressure per gram of the polymer in the dry state, and p is the pressure of penetrant in cmHg. Though only one point is shown in the fiure, the isotherm of carbon dioxide was found to be a straight line in the pressure region studied. That is, Henry's law is obeyed below 1 atm. On the other hand, the isotherm of acetone is convex to the pressure axis over the pressure range studied, i.e. the isotherm is of Type III according to the BET classification.[18]

The very low solubility of carbon dioxide may suggest that in permeation of the
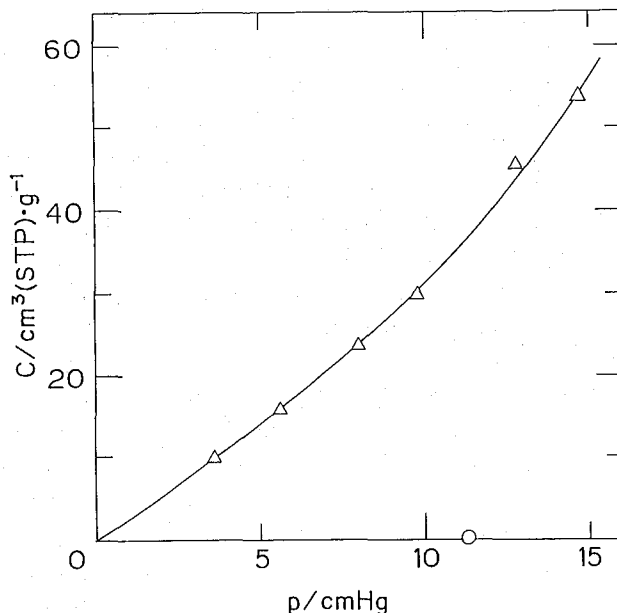

Fig. 1. Sorption isotherms of gas and vapor in poly (vinyl acetate) at 30°C. ○: CO₂, △: acetone vapor.

carbon dioxide/acetone mixture transport behavior of acetone will not be affected by the presence of the parter component. In other words, the permeation characteristics of acetone in the mixed-gas permeation will be the same as those in the pure-gas permeation. On the other hand, it is anticipated that high soluble acetone component will alter the transport behavior of carbon dioxide in the PVAc membrane.

Permeation Behavior

Pressure dependence of the permeability coefficient for acetone $P_{Acetone}$ at 30°C is shown in Fig. 2. Data obtained from pure acetone permeation are represented by unfilled triangles and those from mixed-gas permeation by filled triangles. An unifilled triangle with a vertical bar represents $P_{Acetone}$ estimated from sorption experiments using relation $P = \bar{D}S$, where $\bar{D}$ is the integral diffusion coefficient and S is the solubility coefficient. Absorption and desorption curves at low pressure of acetone were found to be nearly Fickian and an approximate value of $\bar{D}$ was able to be determined from the curves.

As anticipated from the low solubility of carbon dioxide in PVAc, no difference is
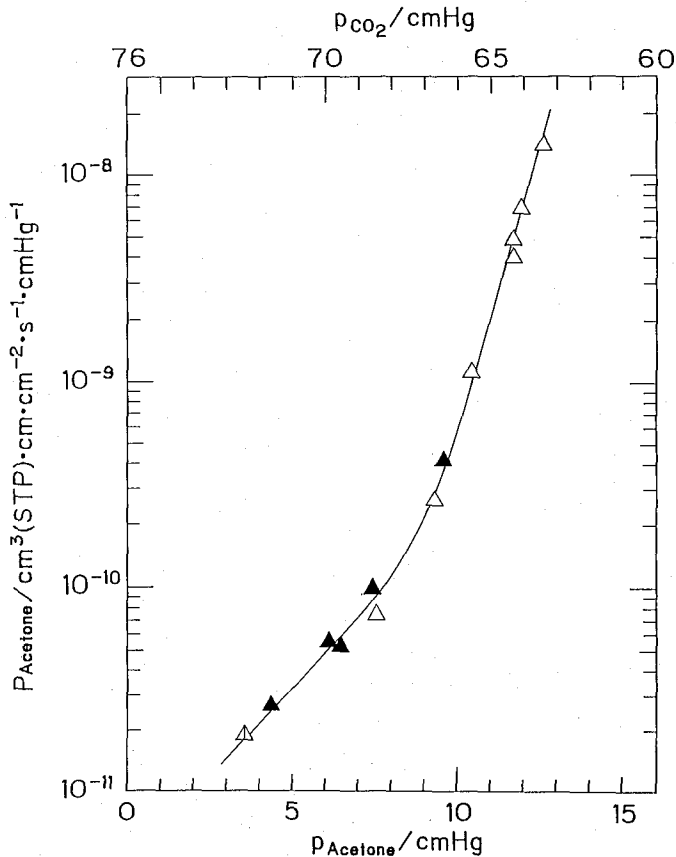

Fig. 2. Dependence of permeability coefficient for actone vapor on partial pressure at 30°C. Total pressure of the gas mixture is 1 atm. △: acetone vapor, pure; ▲: acetone vapor, mixture; ⋏: acetone vapor, pure, from sorption measurements.

observed between the pressure dependence of $P_{Acetone}$ obtained from pure-gas permeation and that from mixed-gas permeation. In the region of low pressure, the logarithm of $P_{Acetone}$ is linearly related to the partial pressure of aetone. With further increase of the partial pressure $P_{Acetone}$ increases rapidly. This indicates that the plasticizing effect of sorbed acetone is not weak. The observed pressure dependence of $P_{Acetone}$ conforms to the prediction of the free-volume model, but not to that of the dual-mode transport model.

Figure 3 shows the pressure dependence of the permeability coefficient for carbon dioxide P_{CO_2} obtained from the pure-gas and the mixed-gas permeation measurements at 30°C. Unifilled and filled circles represent respectively results obtained from permeation measurements with the pure gas and the gas mixture. In permeation of pure carbon dioxide, P_{CO_2} was independent on pressure in the pressure region below 1 atm, though only two points are shown in Fig. 3. P_{CO_2} from permeation measurement with the gas mixture increases with increasing the partial pressure of acetone. This behavior agrees qualitatively with the prediction of the free-volume model described in a previous section.
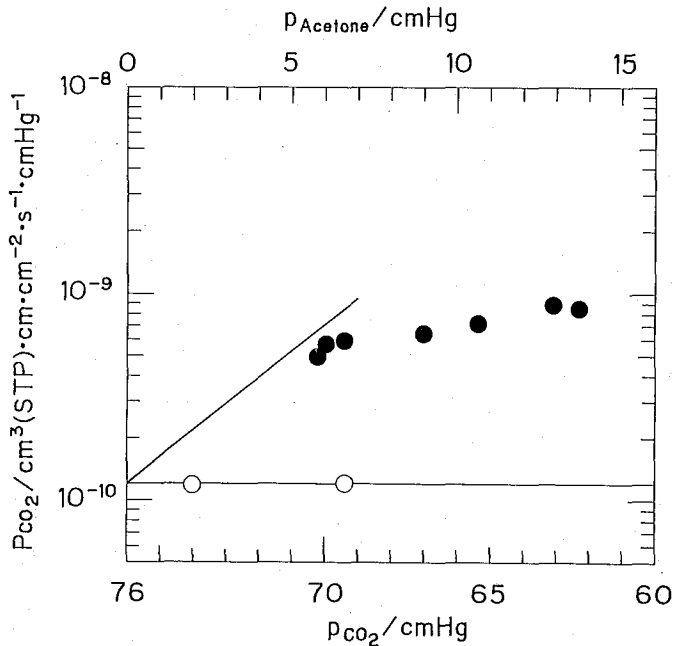

Fig. 3. Dependence of permeability coefficient for carbon dioxide on partial pressure at 30°C.
○: CO_2, pure; ●: CO_2, mixture; —(thick): CO_2, mixture, calculated from Eq. (4).

As seen in Fig. 2, the logarithm of $P_{Acetone}$ correlates linearly with pressure of acetone at low pressures. Therefore, in this pressure region the free-volume model for mixed-gas permeation proposed by Fang et al.[13] may be employed to predict quantitatively values of P_{CO_2} in permeation of the gas mixture. The parameter $m(T)$ for acetone was evaluated from the pressure dependence of $P_{Acetone}$ shown in Fig. 2, and the ratio B_{dA}/B_{dB} was estimated by using molecular diameters of the two component

gases, which were obtained from gas viscosity measurements.[19]   The pressure depend-ence of P_{CO_2} calculated by Eq. (4) is shown in Fig. 3 by a thick line.

It is seen in the figure that Eq.(4) is applicable to predict values of P_{CO_2} at partial pressures of acetone below about 6 cmHg.   With increasing partial pressure of acetone, however, the observed values of P_{CO_2} are lower than those calculated by Eq. (4).   This suggests that acetone molecules sorbed in this pressure region contribute to less extent to the increase of the free volume of the system than that assumed in the free-volume model.   Thus acetone molecules sorbed by the polymer membrane in the temperature region slightly above the glass transition of the system would be not uniformly distributed in the membrane.   It is considered that detailed knowledge about the local structure, and local moleculer motions also, of the penetrant-polymer system on a scale comparable with that of the elementary transport process of a penetrant molecule in the membrane is needed to interpret fully the observed behavrior.

Acknowledgements

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