The Differential Permeation Rate Measurement of Gases in PVAc

K. TOI, M. IZUTSU, A. MIZUSHIMA, T. ITO, and I. IKEMOTO,
*Department of Chemistry, Faculty of Science, Tokyo Metropolitan
University, Setagaya-ku, Tokyo 158, Japan*

Synopsis

The temperature dependence of the CO_2 permeability coefficient in poly(vinyl acetate) (PVAc) was measured continuously by a differential permeation rate method. T_g was changed at upstream pressure in PVAc/CO_2 system, and curious behavior of Ar was observed after CO_2 conditioning. The differential permeation rate experiment successfully exhibits the effect of continuous temperature change for membranes with different histories.

INTRODUCTION

Since thermodynamic equilibrium is virtually never achieved for glassy polymer, many properties may be expected to depend on prior history. Permeation of gas molecules through glassy polymers may be so affected by the history of the polymer. Previously, we reported experimental results that showed when the time scale of the response of molecular movement is approximately the same as the time lag for gas diffusion, the apparent diffusion coefficient D_a calculated from the time lag was affected by physical aging time.[1] As a result, we could not directly apply the dual sorption and mobility model[2] to estimate parameters employed in the model equations.

But with proper precautions, on the contrary, gas molecules are expected to be effective probes for characterizing the physical state of glassy polymers. It is well known that annealing reduces the solubility of gases in the glassy polymer, and exposure of the glassy polymer to a penetrant which swells it causes a dilation of the polymer, which is not immediately reversible on removing the penetrant.[3]

Since the relaxation times for glassy polymers are relatively long, it is difficult to ascertain whether the penetrant and membrane systems studied were in a similar condition during permeation measurement made before and after the above mentioned treatment.

Thus, we have applied a modified technique, or differential permeation rate method, in order to test the attainment of true steady-state and the effect of the annealing and the conditioning. We have observed many interesting phenomena with this experimental method as shown below.

DIFFERENTIAL PERMEATION RATE

Suppose that a membrane is mounted in a permeation cell and two experiments are performed.[4] The first experiment is the integral permeation

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method in which a penetrant permeates through a membrane into a closed chamber, and a signal proportional to the total mass of penetrant in the chamber is monitored continuously, i.e., the pressure p_t in the closed chamber is measured, with the data appearing as the usual transient permeation curve. The second is the differential permeation rate method. The penetrant permeates through the membrane into a flowing stream, which is analyzed as it leaves the permeation cell to yield a signal proportional to the permeation rate. The upstream penetrant activity is the same, but now the rate Φ_t, at which the penetrant emerges into the downstream chamber, is measured directly. This differential permeation rate method yields the signal proportional to permeation rate.

Provided that the downstream surface concentration in the closed volume system remains negligible compared to the upstream concentration, the quantities measured in these two experiments are simply related:

$$p_t = \int \Phi_t \, dt. \tag{1}$$

It follows that

$$\Phi_t = dp_t/dt \tag{2}$$

and, since Φ_t approaches a constant value Φ_∞, the plot of p_t vs. t approaches a straight line of slope Φ_∞.

In the actual experiment, the permeation coefficient can be obtained from the value of Φ_∞ using eq. (1). There are some differences between the exact function p_t and its asymptotic limit, and also between the permeability coefficients from integral method and from the differential method. But, using the ratio of both permeation coefficients, the apparent permeation coefficient can be obtained from Φ_∞.

The differential permeation rate curve $\Phi_t \sim t$ can be obtained from the start of the experiment to extensive time without a considerable change of downstream pressure as seen in the integral method. Integral permeation curves are obtained by the summation of Φ_t by calculation with a computer program. In order to obtain the apparent permeation coefficient, the ratio of integrated values of Φ_t to the apparent usual permeation coefficient was used at a standard temperature and pressure. We confirmed that the apparent permeation coefficients obtained from this method were almost equal at all ranges of experimental conditions.

EXPERIMENTAL

PVAc film was chemically identical to that described earlier.[1] The gas permeation equipment connecting the microcomputer to a GP-IB multimeter was the same as reported previously.[5]

RESULTS AND DISCUSSION

The effect of a different history of the same membrane on the permeation was measured for the PVAc/CO_2 system at 20°C, as shown in Figure 1. The
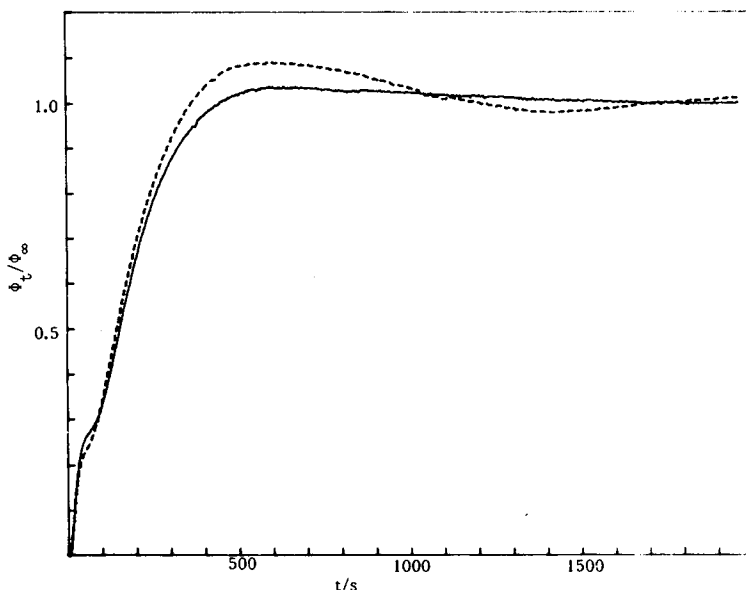
Fig. 1. The reduced differential permeation rate curves with different histories for PVAc/CO_2 system: (- - -) after rapid cooling from 45 to 20°C for 1 h; (—) after CO_2 conditioning.

dotted line shows the experimental result of the sample film which was reached by abruptly cooling by ca. 1.0°C/min from 45°C. The number on the ordinate indicates the ratio of each value Φ_t and the steady state permeation rate Φ_∞. In this case, Φ_∞ is calculated by the mean value of the final 100 points within 2000 points of Φ_t.

After the dotted line experiment, the membrane as being set in the cell was exposed to 1 atm CO_2 pressure for 24 h from both sides at 20°C. The solid line shows the results at the same sequence mentioned above. It is clear that, soon after rapid cooling, the membrane did not reach steady permeation within the observed time. Conditioning in CO_2 prior to measuring erases a portion of the heat treatment history.

Figure 2 shows the integral permeation curves obtained from summation of Φ_t in Figure 1 by calculation with computer program. Both curves, at first sight, seem to reach the steady state. But the shape of the permeation curve was changed by CO_2 conditioning. It is obvious that both the apparent permeation coefficient and the amount of permeation at the apparent steady state region decrease with CO_2 conditioning, the same results as in the normal experiment of our previous paper.[1]

The temperature dependence of apparent permeation coefficients from 10 to 50°C at 1 and 0.2 atm upstream pressures is shown in the form of Arrhenius plots in Figure 3. To avoid overlapping, the curves are drawn by using offset. The curves cooled and heated continuously at a rate of 1°C/h do not show any clear break points but change smoothly over a range of temperature. We confirmed that the shape of the curve at the rate of 1.0°C/h was identical with those at rates of 1.5 and 2.0°C/h. The glass transition temperature T_g for each curve is obtained from the intersect of two lines by least square methods. The calculated temperatures are 29.5°C for 1 atm and 31.4°C for 0.2
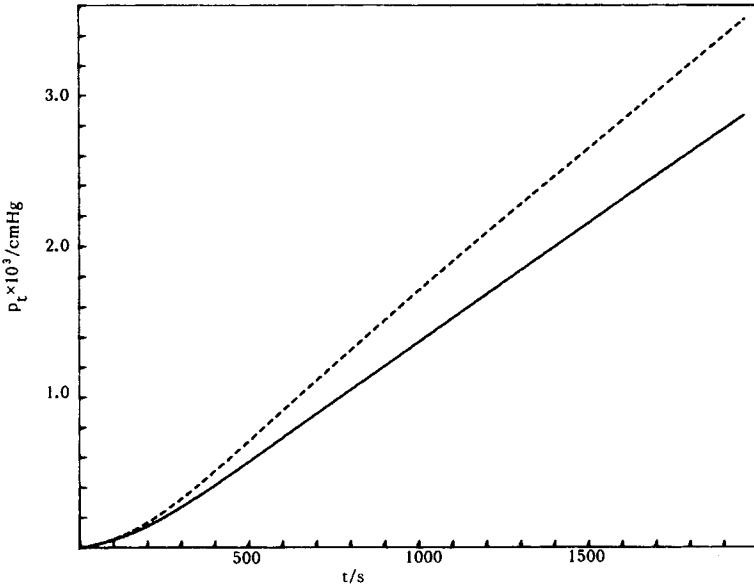
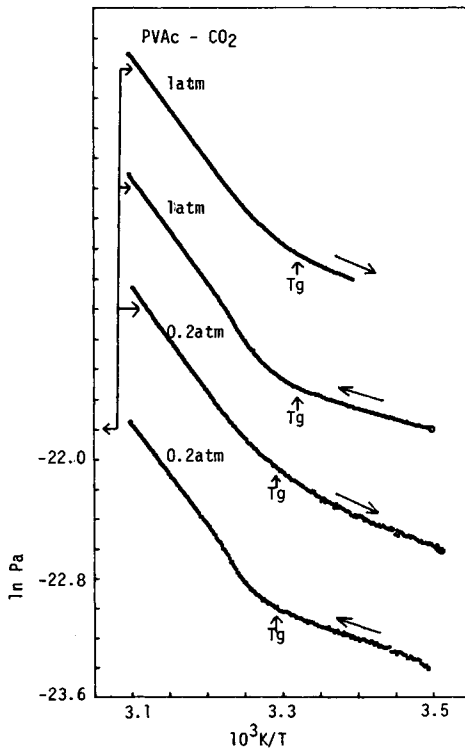Fig. 2. The integral permeation curves obtained by summation of Φ_t of Figure 1. Symbols as in Figure 1.

PVAc - CO_2

1atm

1atm

T_g

0.2atm

T_g

0.2atm

T_g

T_g

ln Pa

−22.0

−22.8

−23.6

3.1   3.3   3.5

$10^3 K/T$

Fig. 3. Arrhenius plots of apparent permeation coefficients from differential permeation rate measurements for PVAc/CO_2 system. Effect of CO_2 pressure on T_g.
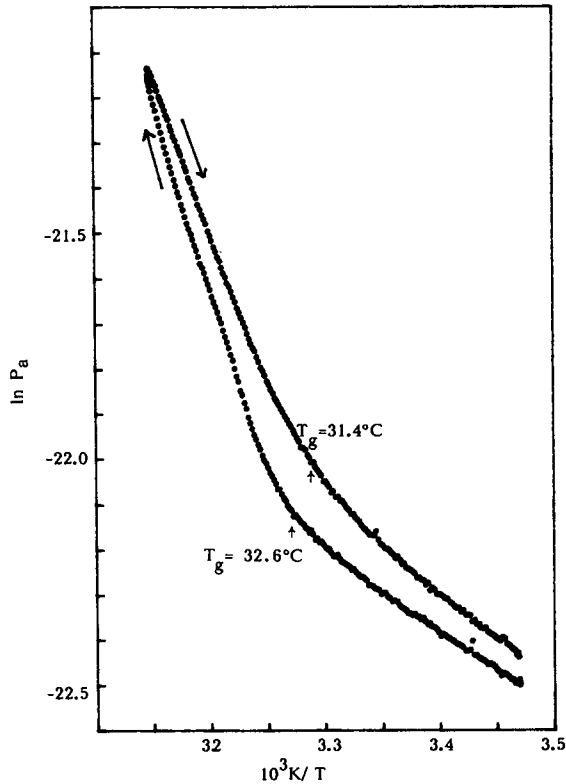
Fig. 4. Arrhenius plots of apparent permeation coefficients from differential permeation rate measurements for PVAc/CO_2 (14 cm Hg) system.

atm. There is a ca. 2°C difference in T_g between the two upstream pressure experiments. It is evident that the CO_2 causes the depression of the T_g as a result of interaction to PVAc. The similar type effects might be produced by conditioning or plasticization, but in this case there is a continuous change of T_g in thickness direction of the PVAc film, and the depression of the T_g is larger at higher upstream pressure. The pressure dependence of the transport coefficients near T_g seemed to involve such an effect.

To investigate the effect of conditioning at 15°C, the film was treated by the same method as mentioned above. As the temperature was changing continually at a rate of 1°C/h from 15°C, the permeation coefficient at 0.2 atm calculated from the differential permeation rate experiment was obtained continuously as shown in Figure 4. After 15 h annealing at 45°C, cooling curve was drawn. The curve shows 31.4°C of T_g and seems to return to the original T_g in Figure 3.

The permeability coefficients of Ar are also measured by the continuous method as shown in Figure 5. The data scatter considerably because of a small permeability coefficient, or a small signal to noise ratio, compared with that of CO_2. But from the curves cooled and heated continuously, almost the same transition temperatures of ca. 32.7°C were scarcely obtained. This value is higher than that of the low pressure of CO_2. This means that T_g keeps higher
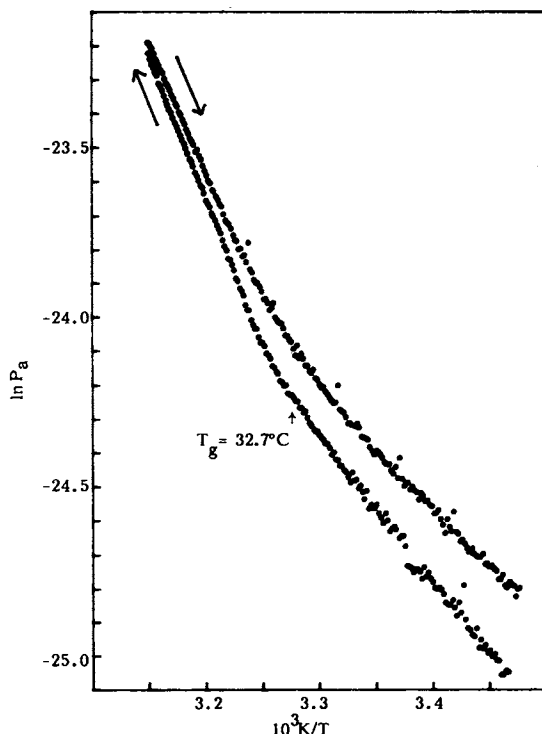
Fig. 5. Arrhenius plots of apparent permeation coefficients from differential permeation rate measurements for PVAc/Ar (70 cm Hg) system before CO_2 conditioning.

values because of no appreciable interaction between the polymer and Ar. The slope difference between above and below T_g is smaller than in the case of CO_2. Further, the difference of activation energy of Ar between rubbery and glassy state is small compared with that of CO_2.

After CO_2 conditioning at 15°C for 24 h, the temperature effect with P_a of argon was measured at the temperature from 15 to 45°C. The results are shown as curve (a) in Figure 6. At a lower temperature, P_a shows abnormally large values. With increasing temperature, a curious curve with maximum and minimum peaks was drawn. After annealing at 45°C for 15 h and then slowly cooling to 15°C, heating curve (b) shows 34°C of T_g, which is higher than before conditioning (in case of CO_2, it showed same values). But these peaks were not reproduced in curve (c) of thicker film. The curve (c) was described by three lines with two intersections without showing the maximum peak such as curve (a) of the thinner film. The shape of this curve gives good agreement with our results for Ar[6] and those of Meares.[7] The values of intersection are calculated as 32.7 and 35.3°C, considerably different from the values of the above references.

The differential permeation rate experiment cannot be expected to obtain an accurate permeation coefficient but can be measured continuously, and especially can exhibit the effect of a continuous temperature change.
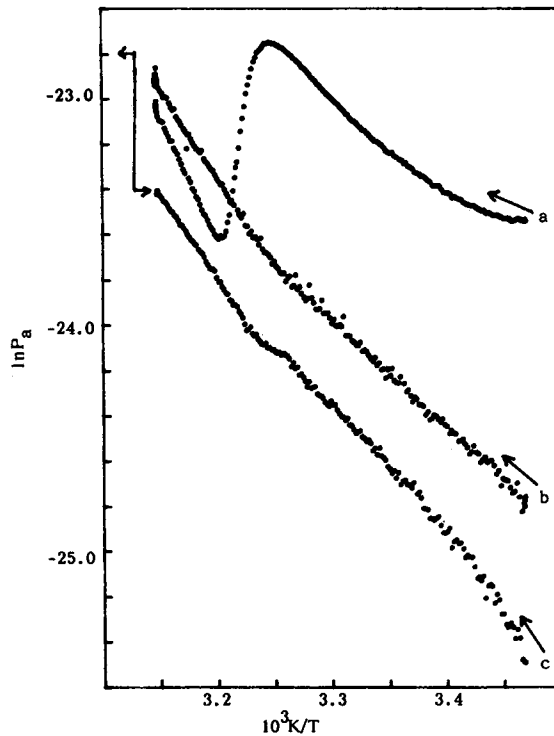
Fig. 6. Arrhenius plots of apparent permeation coefficients from differential permeation rate measurements for PVAc/Ar (70 cm Hg) system after CO_2 conditioning: (a) film thickness = 11.5 $\times$ 10^{-4} cm, upstream pressure = 63.1 cm Hg; (b) film thickness = 11.5 $\times$ 10^{-4} cm, upstream pressure = 56.8 cm Hg (15 h annealing at 45°C after curve a experiment); (c) film thickness = 23.4 $\times$ 10^{-4} cm, upstream pressure = 77.1 cm Hg.

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