

DETERMINATION OF PERMEATION PROPERTIES OF GAS THROUGH POLYMER MEMBRANE BY GAS CHROMATOGRAPHY*

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ABSTRACT

An apparatus constructed for measuring permeation properties of polymer membranes using a mixture of gases is described. A gas chromatographic system was applied to determine the individual transport characteristics of component gases without a vacuum line. This paper also discusses some experimental factors effecting the precision of measurement. The results show that there is a linear relationship between the permeation time and the volume of the gas permeated through the membrane within certain permeation period, which depends on the permeation rate (from 10^{-4} to 10^{-7} cm³ (STP)/cm²·sec·cmHg) of the membrane. The reproducibility has been found to be good with a relative standard deviation of 3.5%. This method is more sensitive, considerably faster and more convenient for determining both the permeability coefficient and the separation factor of a polymer membrane from a chromatogram using mixed penetrant gases.

INTRODUCTION

The permeation of gases through nonporous polymer membranes has been of great interest because of important applications^[1,2]. One of the promising new separation techniques being studied in a number of academic and industrial laboratories is based on the selective permeation, or transport, of fluid through membrane. This technique, in addition to being potentially energy-efficient, requires very simple and compact process equipment and is reliable, safe and easy to control. The permeation process is also useful for the study of polymer structure, morphology, interaction, molecular motion and time-dependent phenomena in macromolecular condensed state. The mechanism of gas permeation has been the subject of numerous investigations.^[3,4] For all these studies an exact measurement of permeation parameters is very essential for studying the relationship between structure and permeability of polymer membranes.

There are many ways to measure the permeability of a polymer membrane, for example, high and low vacuum, volumetric (ASTM) and gas chromatographic methods^[5]. Measuring systems that require a vacuum are usually not sensitive enough, not fast enough, or potentially damaging to the specimen. The gas chromatographic method for measuring gas permeability of a plastic film was first reported by Coskey^[6] and later adopted by Pasternak et al.^[7-10] Experimental techniques and the influence of experimental parameters on the measurement still need careful studies. A gas chromatographic method described in this paper could easily be applicable over a wide range of

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permeation rates. In addition, it would be desirable to be able to measure both the permeability coefficient $\bar{P}$ and the separation factor α based on a chromatogram for mixed penetrant gases. It is much more sensitive and considerably faster than previously reported systems. Results obtained from this method also agree quite well with those from other techniques.

EXPERIMENTAL

A schematic drawing of the apparatus shown in Figure 1 is self-explanatory. The permeation cell F and the gas lines to the cell made of coiled 2mm metal tube were put in a thermostated air bath. The specimen membrane G was clamped between two flat surfaces of the permeation cell, and a rubber ring with a little bit of silicone grease was used as sealant. The circular exposed part of the specimen membrane was of 5cm diameter and the volume of each cell compartment was less than 4cm³. The pressure of penetrant gas in the upstream compartment of the cell is exactly controlled and determined by pressure regulator C and standard pressure gauge D respectively. The downstream compartment of the cell connected the carrier gas line with chromatographic column I and then detector J while the four-way sampling valve H was turned back from the bypass.

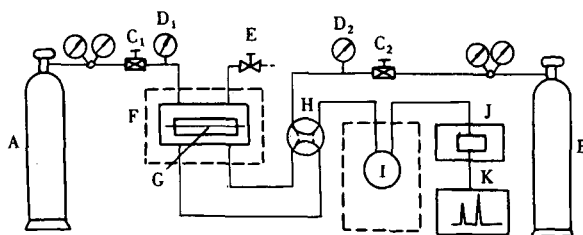


Fig. 1 Schematic drawing of the permeability measurement system

A Penetrant gas cylinder; B Carrier gas cylinder; C Pressure regulator; D Standard pressure gauge; E Flow control valve; F Permeation cell; G Membrane; H Sampling valve; I GC column; J Detector; K Recorder.

During operation the downstream compartment of the cell was first purged by passing the carrier gas and the detector was zeroed. In an actual run, the gas permeated through the specimen membrane was collected in the closed-off cell for a given time interval, meantime the carrier gas being diverted to the bypass. The carrier gas was then switched-back through downstream compartment of the cell, and the permeated gas was picked up by the carrier gas and carried to the gas chromatographic system. In the chromatogram recorded as shown in Figure 2 the area under each chromatographic peak is a measurement of the amount of gas permeated through the membrane during the time interval.

From the chromatographic peak area normalized by standard gas sample, the permeation volume V , at a given temperature T , permeation time t and penetrant gas pressure p , can be obtained. The gas permeability of a planar, homogeneous and isotropic membrane is characterized by a mean permeability, or mass transfer, coefficient $\bar{P}$ which is defined by the isothermal relation^[3].

$$\bar{P} = J\delta = \frac{VT_0 p_{atm} \delta}{atpTp_0} \quad (1)$$

where J is the steady-state rate of gas permeation through unit membrane area when the partial pressure of the penetrant gas in downstream side can be ignored, δ and a represent the effective

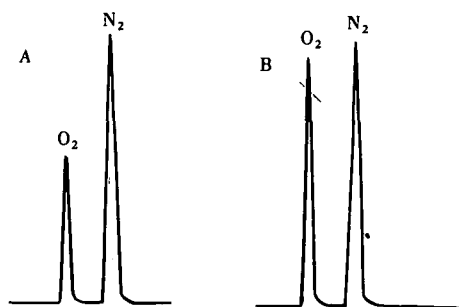


Fig. 2 The chromatograms of air before (A) and after (B) separation by a membrane.

(Column: 5A molecular sieve, 30°C; Detector: TCD)

membrane thickness and area exposed to the penetrant gas, respectively. p_{atm} is the atmospheric pressure, $p_0 = 76$ cmHg and $T_0 = 273$ K. In the case of a mixed penetrant gases A and B with partial pressures p_A and p_B in the upstream compartment respectively, the separation coefficient $\alpha_{A,B}$ is expressed^[4] by

$$\alpha_{A,B} = \frac{\bar{P}_A(1 - p_{A2}/p_{A1})}{\bar{P}_B(1 - p_{B2}/p_{B1})} \quad (2)$$

when the partial pressures p_{A2} and p_{B2} in the downstream compartment are nearly zero, $\alpha_{A,B}$ can be approximately expressed by

$$\alpha_{A,B} = \bar{P}_A / \bar{P}_B \quad (3)$$

RESULTS AND DISCUSSION

Influence of carrier gas on the measurement

Comparing with the vacuum method, the existence of a carrier gas flux in the downstream compartment of the cell is an important factor in the gas chromatographic method. As the penetrant gas is permeating from the upstream side through the membrane, the carrier gas can also be transferred back to the upstream side to form the partial pressure in the upstream compartment of the cell. As mentioned before, the total pressure in the upstream compartment of the cell is kept constant by the pressure regulator system, therefore, the actual pressure p of penetrant gas in the upstream compartment of the cell decreases with increasing permeation time due to the back transfer of the carrier gas. When the permeation rate of the carrier gas (for example hydrogen, helium) is faster than that of the penetrant gas, the influence of the carrier gas on the measurement can not be ignored. In order to correcting this effect, the mixture of penetrant and carrier gas formed in permeation period must be driven out through a valve E in the upstream compartment of the cell with a constant flow rate much larger than the permeation rate of the carrier gas through the membrane, so as to keep fresh penetrant gas in the upstream side. After such a treatment, the actual pressure of the penetrant gas corresponds with the value indicated on the pressure gauge. Figure 3 showed the relationship between the pressure of the carrier gas (hydrogen) and the permeation rate of oxygen (0.6 kg/cm²) through a membrane of thickness $30\mu\text{m}$, $\bar{P}_{O_2} = 3.6 \times 10^{-9}$ cm³ (STP) · cm/cm² · sec · cmHg at 25°C. The data indicate that permeability measurement carried out in this work is independent of the carrier gas pressure in the experimental range.

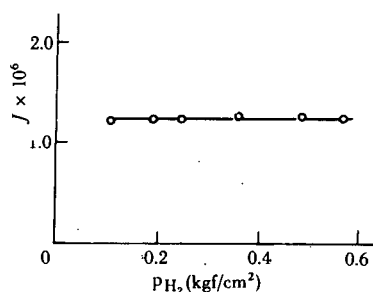


Fig. 3 The relationship between permeation rate and carrier gas pressure

Permeation time

As well known, the steady-state rate of gas permeation through a polymer membrane is a constant when a pressure gradient is maintained across the membrane, and the permeation volume V can be expressed by the isothermal relation:

$$V = KJ(p_1 - p_2)at \quad (4)$$

where K is a coefficient depending on the experimental conditions, p_1 and p_2 are partial pressures of the penetrant gas in the upstream and downstream compartment of the cell respectively. Due to limited volume of the cell compartment the partial pressure p_2 will increase with increasing permeation time. As shown by the relation (4), only when p_2 tends to zero, the permeation volume will be proportional to the permeation time:

$$V \approx KJp_1at = K'Jt \quad (5)$$

where K' is a constant for a given specimen under given measurement conditions. Experimental data indicated that the permeation volume did increase linearly with increasing permeation time within a certain time period only, as shown in Figure 4. The width of the linear range depended on the J value of the membrane, i.e. the higher the J value the shorter the linear range. Therefore the permeation time must be chosen within the linear range for actual measurements.

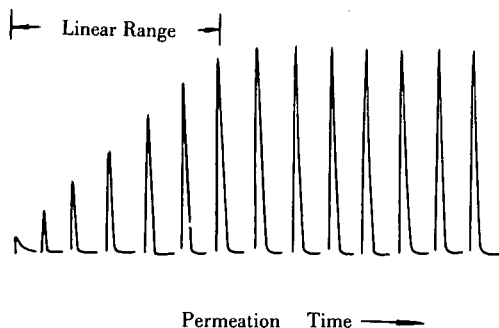


Fig. 4 The chromatographic profiles of gas permeation with various permeation times.

Pressure of penetrant gas

The permeation of a gas through a nonporous polymer membrane can be induced by a pressure gradient and is believed to occur by molecular diffusion process. So the permeation volume for unit area and time is proportional to the pressure difference across the membrane

interfaces:

$$V \propto p_1 - p_2 \quad (6)$$

If there are some pin holes and channels across the membrane, transference of gas would occur by both diffusion and flow (including molecular flow and viscous flow for different sizes of pores)⁽¹⁰⁾. However, permeation volume depended not only on the partial pressure of the penetrant gas, but also on the total pressure in the upstream compartment of the cell. In this case, a nonlinear relationship between V and p will be found as shown in Figure 5, which can be used to confirm the existence of holes across the membrane.

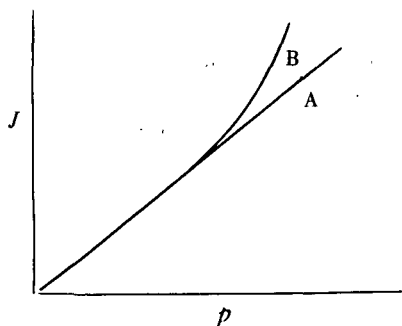


Fig. 5 The pressure dependence of gas transmission rate for diffusion (A) and diffusion plus flux (B) mechanisms.

For determinations with a multicomponent penetrant gas, the permeability coefficients $\bar{P}_A$ and $\bar{P}_B$ of each gas component A and B through a membrane could be calculated from the partial pressures p_A, p_B in the penetrant gas mixture and the separated chromatographic peaks (as Figure 2). It is evident that if the permeation rate of the component A is higher than that of the component B, i. e. $J_A > J_B$, the relative concentration of the component A in the upstream compartment of the cell will decrease during the permeation period. That will cause some change of the composition of the penetrant gas mixture. So it is important to maintain a continuous efflux of the penetrant gases through the valve E (see Figure 1) to keep a constant composition in the upstream side. Then both $\bar{P}_A$ and $\bar{P}_B$ can be exactly determined from a chromatogram for the multicomponent penetrant gases.

Separation coefficient

Usually the separation coefficient $\alpha_{A,B}$ for gases A and B can be obtained from a determination of $\bar{P}_A$ and $\bar{P}_B$ separately. In the gas chromatographic method, the separation coefficient could be directly calculated from the ratio of corrected peak areas on a chromatogram, as compared to the original composition of the multicomponent penetrant gases. Based on the relations (1) and (3), we have

$$\alpha_{A,B} \approx \bar{P}_A / \bar{P}_B = \frac{V_A p_B}{V_B p_A} \quad (7)$$

Obviously, this method is much more convenient and considerably faster than previously reported methods. Results of separation coefficient obtained from chromatograms also showed good agreement with those from vacuum, volumetric and gas concentration measurements. A small difference of the α value between the measurements using multicomponent and individual penetrant

gases may be caused by the local concentration change of the multicomponent gas at the membrane interfaces as mentioned before. Fortunately, this situation is even closer to the practical separation process of gas mixtures, and, perhaps, more meaningful to the application of polymer membranes.

Reproducibility and applications

A number of homogeneous and unsymmetrical polymer membranes, including glassy and rubbery materials, with thicknesses ranging from 3μm to 50μm have been measured by gas chromatographic method described in this paper. The data obtained indicate that the method here presented is the most suitable one to over a wide permeability range from 10⁻¹² to 10⁻⁶ cm³(STP).cm/cm².sec.cmHg. The high sensitivity of chromatography is convenient for measurements on samples of very low permeation rates. On the other hand the membranes with high permeation rates are more important for practical applications. To our experience, the highest permeation rate value so far measured by the present method is 3 × 10⁻⁴ cm³(STP)/cm².sec.cmHg with good reproducibility, as shown in Figure 6.

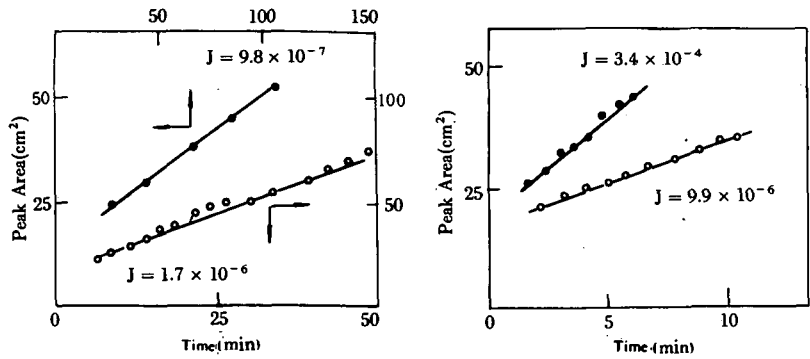


Fig. 6 The illustrations of chromatographic measurement with different permeation rate range.

For instance, the $\bar{P}_{O_2}$, oxygen permeability coefficient, of a standard polystyrene film (offered by Japan Membrane Society, thickness 50μm) was determined to be $\bar{P}_{O_2} = 1.82 \times 10^{-10}$ cm³(STP).cm/cm².sec.cmHg, at 20°C, which is in good agreement with the reference data (1.8×10^{-10} cm³(STP).cm/cm².sec.cmHg, by Japan Membrane Society) and the value

Table 1 Experimental reproducibility*

GC Peak Area(cm ²)				Average	$\sigma = \sqrt{\frac{\Sigma d_1^2}{n-1}}$	$\sigma \%$
Experimental						
436.50	425.25	429.75	459.00	419.66	14.8	3.5
425.75	400.50	409.50	427.50			
423.00	400.50	414.00	409.50			
409.50	409.50	414.00	420.75			

* penetrant gas: oxygen, 0.7kg/cm²; carrier gas: hydrogen, 0.6kg/cm²; permeation temperature: 18°C; permeation time: 60 sec; column: 5Å molecular sieve; detector: TCD; $\bar{P}_{O_2} = 7.4 \times 10^{-9}$ cm³(STP) cm/cm².sec.cmHg.

obtained by the vacuum method ($1.9 \times 10^{-10} \text{cm}^3(\text{STP}) \cdot \text{cm} / \text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$). For some polydimethyl siloxane membrane samples of thickness of 5—10 μm , which were made from soaking a microporous polypropylene supporter in the polysiloxane solution and drying under vacuum, the determined values of oxygen permeability coefficient $\bar{P}_{O_2}$ and separation coefficient for oxygen/nitrogen $\alpha_{O_2.N_2}$ are $6.1 \times 10^{-8} \text{cm}^3(\text{STP}) \cdot \text{cm} / \text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ and 2.10 respectively. The values are in good agreement with those from vacuum and oxygen concentration measurements.

Finally, the experimental reproducibility is illustrated by the data summarized in the above table which were measured from a solution casted membrane of polyester-polyether segmented copolymer, the thickness being 30 μm . The reproducibility is good with a relative standard deviation of 3.5%.

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