

Experimental Estimation of Gas-Transport Properties of Linear Low-Density Polyethylene Membranes by an Integral Permeation Method

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ABSTRACT: In recent years, we have investigated gas-transport phenomena in coextruded linear low-density polyethylene (LLDPE) membranes. For the most part, coextruded LLDPE membranes were investigated because of their excellent mechanical properties, which explain their extensive use in the packaging industry. Because of the small thickness of coextruded LLDPE membranes, significant errors can be involved in the determination of the diffusion coefficient of gases in the membranes by the time-lag method. To obtain more precise transport parameters for LLDPE membranes, we determined the permeability and diffusion coefficients for O₂, CO₂, He, and N₂ from 298 to 348 K by employing an alternative method recently developed. The results indicate that the procedure used in this study for determining the diffusivity of gases in membranes was precise and more efficient than a method based on the evaluation of the time-lag parameter. With respect to permeability, the coefficients obtained in this work agree satisfactorily with those obtained by the time-lag method. In general, the permeability and diffusivity results are in satisfactory agreement with the literature values reported for semicrystalline polyethylene membranes. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3013–3021, 2001

Key words: linear low-density polyethylene (LLDPE); membranes; gas; permeability; diffusivity; coextrusion

INTRODUCTION

It is generally accepted that the permeation of gases through dense membranes is a mass-transport process that involves the sorption of a gas into one interface of a membrane, the diffusion of the gas into the membrane, and, finally, its desorption at the opposite interface.^{1–4} According to this interpretation, the transport of gases across a membrane can be described in terms of three coefficients. The permeability coefficient P is used

to describe the overall transport of gas across the membrane, whereas the diffusion coefficient D refers to the movement of the gas molecules inside the membrane, and the solubility coefficient S is used to describe the equilibrium between the gas dissolved in the membrane and the gas in contact with the membrane. The diffusion coefficient is a kinetic factor and is largely determined by polymer–gas dynamics. However, the solubility coefficient is thermodynamic in nature and is affected mainly by polymer–gas interactions.^{5,6}

Diffusion coefficients can be obtained from the kinetics of gas sorption in the membrane or from time lags associated with transient permeation across the membrane.^{7,8} Techniques employing transient permeation measurements are often

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used by membrane technologists⁹ to obtain diffusion coefficients, whereas investigators working on developing foaming processes use sorption kinetics for that purpose.

In the time-lag method, the experiments are conducted in a membrane that is initially evacuated, and the amount of gas that diffuses through the membrane is calculated from the pressure rise in the downstream compartment. If certain initial and boundary conditions are satisfied, the flow through the membrane asymptotically approaches the steady-state flow, and the diffusion coefficient can be determined from the intercept of the asymptote of the pressure–time curve with the time axis, that is, the so-called time-lag parameter.^{10,11} However, the initial and boundary conditions are only approximately satisfied, and these assumptions lead to systematic errors that, in many cases, are not negligible. Modified time-lag methods have been proposed^{12–14} that permit the elimination of some of the error sources, but the error associated with the determination of the time-lag parameter is still present. The measured time lag includes contributions of many response times, and in the case of small time-lag values, for example, if the membrane is thin and/or the diffusion coefficient is large, the magnitudes of these delays can represent a substantial portion of the total response time, and the potential for error in the estimation of the time-lag parameter is considerable.

Therefore, in the case of thin membranes, it would be convenient to find a method that enables the estimation of the diffusion coefficient with less uncertainty. Recently, new approximate methods for the determination of membrane permeability and diffusivity were considered by Nguyen and coworkers;^{15,16} these methods are based on new and more general solutions of Fick's diffusion equations. It seems that the solutions derived by these authors have several advantages in practical use. For example, the gas diffusivity for thin membranes can be estimated with integral permeation measurements, without the necessity of measuring the time-lag parameter. In view of these facts, it was felt that one of the methods developed by Nguyen et al. appeared to be suitable for evaluating the gas diffusivity for coextruded linear low-density polyethylene (LLDPE) membranes. As was shown in a previous article,¹⁷ significant errors were involved in the determination of the diffusion coefficient of gases in LLDPE membranes by the time-lag method, arising from the small thickness of the mem-

branes. The smaller the thickness is, the lower the time-lag parameter is, and, consequently, the larger the uncertainty of the value of the diffusion coefficient obtained by this method is. Even in the most favorable cases, the error in the diffusion coefficient was about 100%.

The main purpose of this article is to test the method by Nguyen and coworkers^{15,16} for the determination of gas-transport parameters in thin films, such as LLDPE membranes, giving special emphasis to the analysis of errors in the evaluation of these parameters. We investigate the gas-transport properties of coextruded LLDPE membranes by studying the temperature dependence of the permeability and diffusion coefficients of various gases in the membrane, with the aim of comparing data obtained in this study with those obtained by other methods.

EXPERIMENTAL

Membranes

Permeation measurements were performed with a dense membrane made of copolymers of ethylene and 1-octene with roughly an 8 mol % content of the latter comonomer. The membrane was prepared by coextrusion with three extruders at different speeds, which gave a membrane made of three layers: A (15 wt %), B (70 wt %), and C (15 wt %). Layers A and B were Dowlex 2247 ($\rho = 0.917 \text{ g cm}^{-3}$), and the third layer (C) was Dowlex 2291 ($\rho = 0.912 \text{ g cm}^{-3}$). The resulting thickness of the membrane was 20 μm .

The thermograms of the membrane, obtained with a PerkinElmer DSC-4 calorimeter at a heating rate of 8°C min^{-1} , exhibited a simple and broad melting peak, whose departure from the baseline and maximum were located in the vicinity of 60 and 120°C , respectively. The degree of crystallinity of the membrane, determined by calorimetry, amounted to 25%. A more detailed analysis of the morphology of the membrane, carried out by Raman spectroscopy, gave 0.24, 0.60, and 0.16 for the values of the crystalline, amorphous, and crystalline–amorphous interface fractions, respectively. As a result of the processing conditions, the membrane was oriented in the direction of extrusion, as indicated by its birefringence ($\Delta n = 1.4 \times 10^{-3}$).

Gas-Permeation Experiments

Gas-transport properties of the LLDPE membrane were evaluated with the experimental

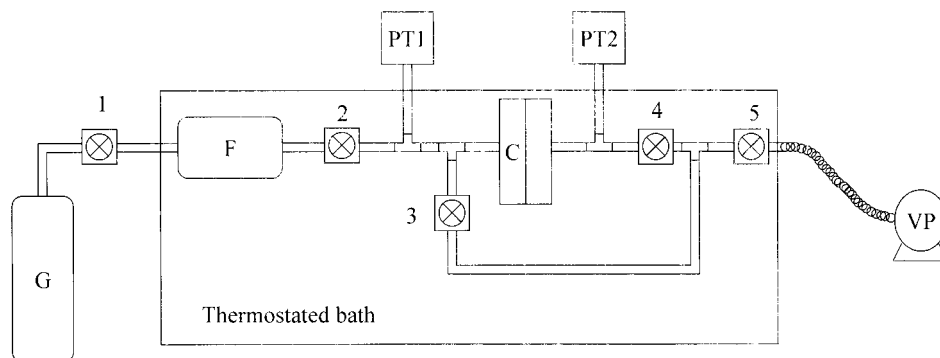


Figure 1 Schematic diagram of the experimental setup for the gas permeation measurements. PT1 and PT2 represent the pressure sensors, G is the gas supply, F is the feed reservoir, C denotes the membrane cell, VP is the vacuum pump, and the numbers 1–5 denote valves.

setup shown as a schematic diagram in Figure 1. The main part of the permeation apparatus was a cell with the membrane and pressure transducers. The cell we used was a flat-sheet type, and it consisted of two cylindrical pieces made of stainless steel. The membrane inserted in the cell was supported by a porous metal disk to ensure only a small change in the effective area and thickness variation when gas pressure was applied. The pressure was measured with two capacitance pressure transducers, PT1 and PT2, with 10^3 and 10^2 Torr, respectively. The pressure of the gas in the downstream compartment was measured by PT2, and it was converted into electrical signals and automatically recorded as pressure data with a personal computer (PC).

Experiments were conducted at different temperatures by the immersion of the permeation apparatus into water contained in a thermostated bath. The experiments were performed over the temperature interval 298–348 K, and the temperature was kept within $\pm 0.1^\circ\text{C}$ of the selected temperature.

The determination of the transport parameters in the LLDPE membrane was conducted according to one of the new methods recently suggested by Nguyen et al.¹⁵ The integral measurement method described by these researchers permits us to evaluate the permeability and diffusivity of gases in a membrane with knowledge of the time evolution of the pressure difference across the membrane. Before the measurement is begun, the pressures of the gas on the two sides of the membrane must be set equal. At the beginning of the measurement, a higher and constant pressure is applied on the upstream pressure side of the

membrane, and the downstream compartment is closed. The measurement consists of following the increase in pressure in the downstream side as a function of time, $p(t)$. The amount of gas, $Q(t)$, that has permeated through unit surface area of the membrane can be obtained from the pressure rise:

$$Q(t) = \frac{T_N V_d}{A T p_N} [p(t) - p(0)] \quad (1)$$

where $p(t)$ and $p(0)$ are the pressures in the downstream side at time t and at the beginning of the measurements, respectively; T_N and p_N are the standard temperature and pressure, respectively; V_d is the volume of the downstream compartment; A is the membrane area; and T is the experiment temperature. If the gas accumulation in the downstream compartment is related to the diffusion flux in the membrane by a mass balance equation, the following equation can be written:

$$\frac{d(\ln \Delta p)}{dt} = -\frac{p_N A T}{V_d l T_N} P \quad (2)$$

where Δp is the pressure difference between the two sides of the membrane in the steady state of diffusion and l is the membrane thickness. By rewriting the latter equation, one can determine the permeability coefficient by the following equation:

$$P = \frac{T_N V_d l}{T p_N A} \beta \quad (3)$$

where β is a parameter that is evaluated from

$$\beta = -\frac{\partial \ln(\Delta p)}{\partial t} \quad (4)$$

It follows from the work by Nguyen and coworkers^{15,16} that the diffusion coefficient can be determined from the asymptote Q_a of the experimental function $Q(t)$. These investigators showed that Q_a can be expressed by the following equation:

$$\begin{aligned} \frac{Q_a}{C_0 a l} + \frac{1}{3} [1 - \exp(-\beta t)] + \frac{1}{6} \\ = \frac{D}{\beta l^2} [1 - \exp(-\beta t)] \end{aligned} \quad (5)$$

where C_0 is the gas concentration in the upstream membrane surface and a is an experimental parameter. For experimental measurements with thin membranes such as coextruded LLDPE, resulting in a very short time lag, one can obtain the diffusion coefficient without evaluating the intercept of the asymptote Q_a with the time axis, because by combining eqs. (3) and (5) and Henry's law, we can write

$$\begin{aligned} D = \beta l^2 \left\{ \frac{1}{6} + \frac{1}{3} [1 - \exp(-\beta t)] \right\} \\ \times \left[1 - \exp(-\beta t) - \frac{A Q_a T p_N}{a V_d T_N p_0} \right]^{-1} \end{aligned} \quad (6)$$

where t is the steady-state time, p_0 is the upstream pressure, and the parameter a can be estimated from

$$\alpha = 1 - \frac{p(0)}{p_0} \quad (7)$$

The following experimental procedure was adopted. The membrane sample, mounted in the diffusion cell, was initially freed from dissolved atmospheric gases by evacuation for at least 5 days until a minimum volume of desorption gases was obtained. Then, for comparative purposes, the membrane was annealed at 353 K for 24 h before the evaluation of transport properties. This appeared to be adequate to standardize its history. After that, with reference to Figure 1, the test gas was allowed to enter the thermostated area by filling the reservoir F, whereas valves 3, 4, and 5 were open and valve 2 was closed. We

usually left the gas in the reservoir for 2 h. During this time, the upstream and downstream compartments of the cell were under vacuum. Then, to start a run, we exposed both sides of the membrane to a known pressure of the gas. Valve 5 was closed, and valve 2 was carefully opened and closed. After valve 2 was closed, a key at the PC keyboard was pressed, and the signal from the pressure transducer PT2 was recorded as a function of time in a file for a later evaluation. Once the membrane and the gas reached an equilibrium state, indicated by no variation in the reading of pressure from PT2, valves 3 and 4 were closed. Valve 2, which separated the reservoir from the cell, was rapidly opened and closed, and the upstream chamber reached the desired pressure nearly instantaneously at the temperature of the measurement. The opening of this valve was taken as zero in the timescale. Because the upstream pressure had to be constant during the experiment, we carefully operated valve 2 to introduce gas into the upstream chamber of the cell throughout the experiment. In the worst scenario, the fluctuations in the upstream pressure value were 0.3%.

All measurements were conducted three times, and all permeability and diffusion coefficients given represent the average values calculated. All measurements were performed with a pressure difference between the two membrane sides of about 760 Torr.

Error Analysis

To calculate P and D , we needed to measure five variables: the pressure difference between the two sides of the membrane, the temperature of the experiment, the volume of the downstream compartment, the membrane permeation area, and the membrane thickness.

The cell was immersed in a constant-temperature bath that could be maintained within 0.1 K of the desired temperature. The volume of the downstream chamber was measured with the helium expansion technique, and the error in its determination was about 3%. The area of the membrane was assumed to be the same as that of the O-ring opening in direct contact with the sample. Because the O-ring area was calculated from the measurement of its inner diameter, the error in the membrane area determination was negligible. The thickness of the membrane was measured with an LVDT Instron 8200 transducer with a precision of 1 μm . The thickness used in

the computation of the permeability and diffusion coefficients was a mean value of 15–20 random measurements, and the deviation from the mean was found to have a spread of $\pm 0.5\%$. The accuracy of the measurements of the pressure difference between the two sides of the membrane depended on the transducer accuracy and precision. The precision of the pressure transducer measurement depended on the reading. The upstream pressure was read with a precision of ± 1 Torr, and the pressure in the downstream compartment was read with a precision of ± 0.01 Torr. Accordingly, because the pressure difference across the membrane was usually 760 Torr, the error in its determination did not exceed $\pm 0.3\%$.

One can see from eq. (3) that the error in the determination of P was due to errors in the measurement of the five variables mentioned previously and the error in the evaluation of the parameter β . The error of β depended on the error of the experimental evaluation of the pressure difference between the two sides of the membrane and the linear fitting of $\ln(\Delta p)$ versus t . As the linear regression of $\ln(\Delta p)$ versus t introduced only a little error, it could be concluded that the error in the determination of β was mainly due to the error in the measurement of the pressure difference across the membrane. In view of the errors involved in the determination of P , we can write

$$\left(\frac{s_P}{P}\right)^2 = \left(\frac{s_\beta}{\beta}\right)^2 + \left(\frac{s_A}{A}\right)^2 + \left(\frac{s_l}{l}\right)^2 + \left(\frac{s_T}{T}\right)^2 + \left(\frac{s_{V_d}}{V_d}\right)^2 \quad (8)$$

where s_i is the standard error of the quantity i . It follows that the relative error in the estimation of the permeability coefficient was about 6%.

For the diffusion coefficient, from eq. (6) we see that the accuracy depended on the experimental determination of β , the relative error in the evaluation of the membrane thickness, the error in the measurement of the pressure difference between both sides of the membrane, and the choice of the steady-state time t for the estimation of D . It then follows that

$$\left(\frac{s_D}{D}\right)^2 = \left(\frac{s_\beta}{\beta}\right)^2 + \left(\frac{s_l}{l}\right)^2 + \left(\frac{s_p}{\Delta p}\right)^2 + \left(\frac{s_t}{t}\right)^2 \quad (9)$$

In this case, the major source of error was the choice of the steady-state time parameter. How-

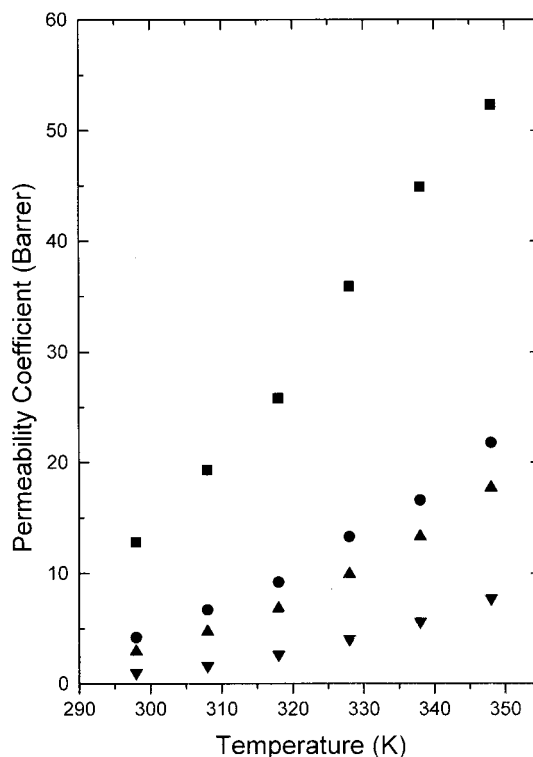


Figure 2 Temperature dependence of the permeability coefficient of (▲) oxygen, (■) carbon dioxide, (▼) nitrogen, and (●) helium through coextruded LLDPE membranes.

ever, the use of the steady-state time parameter instead of the time-lag parameter was advantageous because the relative error of the steady time caused by all time delays (due to the apparatus, the membrane itself, and the experimental procedure) was negligible. Although Nguyen et al.¹⁶ recommended choosing a steady time not too large, we estimated the influence of this choice in the determination of D and found that the diffusion coefficient values varied by 7%, depending on the steady time selected. Therefore, the accuracy of our D determination was about 9%.

RESULTS AND DISCUSSION

We investigated the mass-transport characteristics of coextruded LLDPE membrane by studying the temperature dependence of the permeability and diffusion coefficients of some representative gases in the membrane. For comparative purposes, the temperature dependence was investigated from 298 to 348 K. The permeation results can be observed in Figure 2, where the values of

the permeability coefficient of oxygen, carbon dioxide, nitrogen, and helium as a function of temperature are shown. The permeability coefficient increases with temperature for all gases. For example, the value of P for oxygen in barrers goes from 2.9 to 17.7 when the temperature increases from 298 to 348 K. The temperature is a more significant factor in controlling the gas permeation than the pressure. The effects of temperature and pressure on the transport properties of the LLDPE membranes were reported elsewhere.¹⁸ Permeation results indicate that the temperature has a noticeable influence on gas permeation through the membrane because a small increase in the temperature gives rise to an important increase in the permeability. However, if the pressure difference across the membrane is varied by 2 orders of magnitude, the permeability only exhibits a relatively small change. Nonetheless, the permeability of the gases used in this study increases in the following order, $P(\text{CO}_2) > P(\text{He}) > P(\text{O}_2) > P(\text{N}_2)$, at all temperatures studied. For example, the values of P for these gases at 298 K are 12.8, 4.2, 2.9, and 0.98 barrer, respectively. Literature values¹⁹ of the permeability coefficient of these gases in low-density polyethylene (LDPE) at 298 K are, respectively, 12.6, 4.9, 2.9, and 0.97 barrer. Our values are in excellent agreement with the literature values.

The curves depicting the dependence of the diffusion coefficient on temperature for oxygen, carbon dioxide, nitrogen, and helium, shown in Figure 3, exhibit a similar pattern. For all gases, the diffusivity increases with increasing temperature. As an example, the value of D for O_2 goes from 4.9×10^{-7} to $3.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ when the temperature increases from 298 to 348 K. The diffusion coefficient of helium is 1 order of magnitude larger than those of the rest of the gases, whose values are nearly the same. The permeability coefficient indicates the volume of gas passing through the membrane per second, and the diffusion coefficient determines the speed with which equilibrium conditions are achieved. The diffusion coefficient is dependent both on the size of the gas molecule and on the polymer structure of the membrane. Accordingly, it is expected that the diffusivity of helium will be considerably larger than those of the other gases, in view of its small kinetic diameter compared with those of the rest of the gases studied.²⁰ The diffusion coefficients of the gases used in this study increase in the following order: $D(\text{He}) > D(\text{O}_2) \geq D(\text{CO}_2) \geq D(\text{N}_2)$. The diffusion coefficient values of these

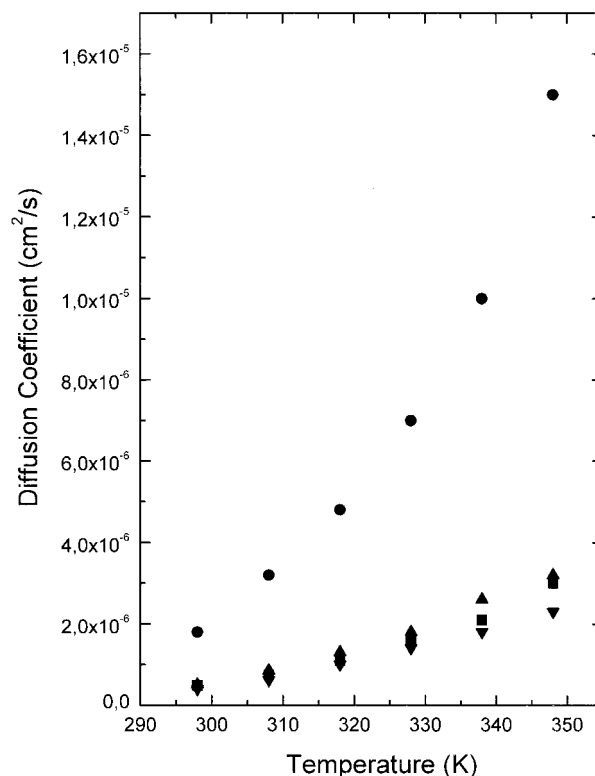


Figure 3 Temperature dependence of the diffusion coefficient of (▲) oxygen, (■) carbon dioxide, (▼) nitrogen, and (●) helium through coextruded LLDPE membranes.

gases are 1.8×10^{-6} , 5.1×10^{-7} , 4.9×10^{-7} , and $4.0 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 298 K. These results are comparable with literature data values¹⁹ for an LDPE with similar crystallinity; diffusivity values for these gases of 6.8×10^{-6} , 4.6×10^{-7} , 3.7×10^{-7} , and $3.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 298 K have been reported. The fact that the ranking of permeability is not the same as that of diffusivity suggests that the solution process of the gases in the membrane plays a leading role in mass transport across the membrane, as discussed previously.¹⁸

The permeation properties in amorphous polymeric membranes are thermally activated processes; that is, their temperature dependence follows an Arrhenius-type behavior:

$$X = X_0 \exp\left(-\frac{E_x}{RT}\right) \quad (10)$$

where X can be either permeability or diffusion coefficients, X_0 is a pre-exponential factor, E_x is the activation energy, R is the gas constant, and T

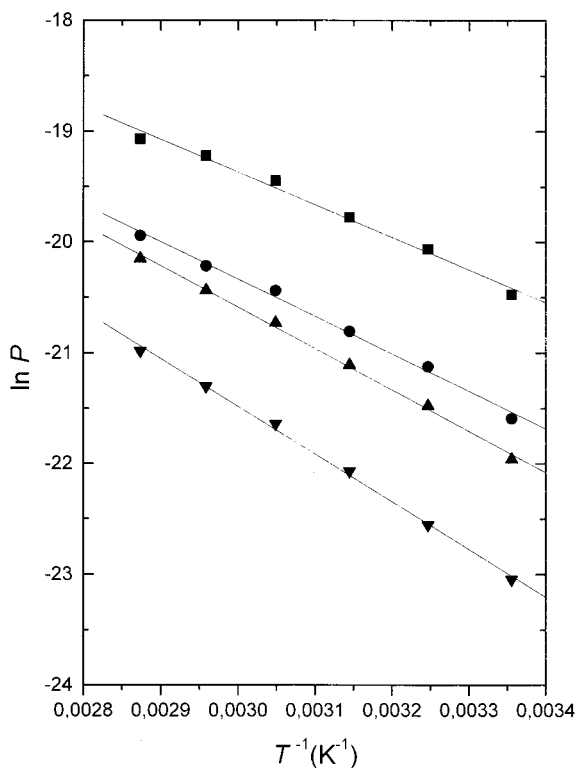


Figure 4 Arrhenius plots of the permeability coefficient of (▲) oxygen, (■) carbon dioxide, (▼) nitrogen, and (●) helium in coextruded LLDPE membranes from 298 to 348 K.

is the gas temperature. The activation energy of permeation is the sum of the activation energy of diffusion and the heat of sorption. The activation energy of diffusion depends on the chain mobility and the size of the penetrant relative to the intramolecular and intermolecular polymer chain gaps. Diffusion coefficients in membranes always increase with increasing temperature; that is, E_D is positive. In most membranes, gas solubilities decrease with increasing temperature; that is, the heat of sorption is negative. Consequently, $E_P/E_D > 1$.

Activation energies associated with these processes can be determined from semilogarithmic plots of the permeability and diffusion coefficients against the reciprocal of the absolute temperature. The Arrhenius plots for the permeability coefficient of oxygen, carbon dioxide, nitrogen, and helium in an LLDPE membrane fit fairly well to straight lines, as reflected by the high correlation coefficients obtained, which lie in the range 0.99–0.999. The fitting of the diffusivity results to straight lines is also satisfactory, as indicated by correlation coefficients of 0.99–0.999. The Ar-

rhennius plots are summarized in Figures 4 and 5, and the activation energy values associated with the transport of the gases in an LLDPE membrane are collected in Table I. The interpretation of the temperature dependence of the permeability and diffusion coefficients could be done in a slightly different manner. A close inspection of the Arrhenius plots suggests that the temperature dependence of the transport coefficients could be divided in two intervals. The break temperature of these intervals would correspond to an α -relaxation process detected in these polymers by thermomechanical techniques.²¹ This fact would enable the fitting of the transport coefficients to two straight lines, thus improving the correlation coefficients up to 0.9999.

To perform a comparative analysis of the procedure proposed by Nguyen and coworkers^{15,16} and the time-lag method, we carried out time-lag experiments to determine both the permeability and diffusion coefficients of carbon dioxide in the same LLDPE sample. In Figure 6, the permeability values obtained with the two methods are presented together. There is a slight discrepancy

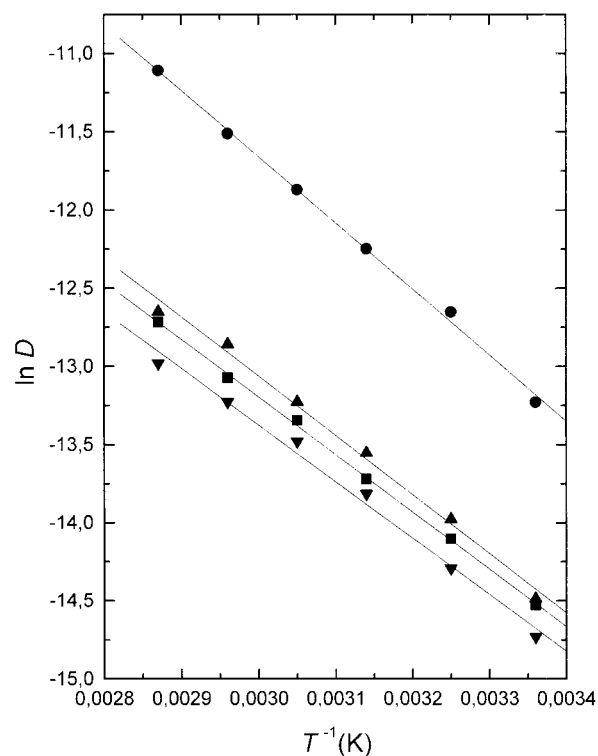


Figure 5 Arrhenius plots of the diffusion coefficient of (▲) oxygen, (■) carbon dioxide, (▼) nitrogen, and (●) helium in coextruded LLDPE membranes from 298 to 348 K.

between the two sets of data. The permeabilities by the Nguyen method are larger than those obtained by the time-lag method. Let us assume that temperature and pressure difference data are measured with sufficient accuracy. Then, all the other deviations can be assigned to the erroneous determination of the membrane thickness and its effective area and the wrong determination of the volume of the lower compartment of the cell. As we mentioned in the Experimental section, their effect on the determination of P is defined by eq. (3). For example, at 298 K, the value we obtained for the permeability coefficient of carbon dioxide is 12.8 barrer, whereas the value reported by the time-lag method is 11.0 barrer. For this latter value, V_d/A should be 0.86 times smaller. Such an error is not likely. The reason for the difference between the two sets of permeability data has to be assigned to other phenomena. This can be attributed to the accuracy of the permeability obtained by the time-lag method. According to Nguyen and coworkers, the time-lag estimation of the permeability coefficient is exactly valid when $\beta \rightarrow 0$, but in practice, $\beta > 0$, so the thinner the membrane is, the larger the error is in the permeability coefficient obtained by the time-lag method. Consequently, the permeability coefficient in thin membranes, such as coextruded LLDPE membranes, would be lower than its true value. With this consideration, the agreement between the two sets of data is deemed to be good enough.

A comparison of the diffusivity values obtained with the Nguyen procedure and those obtained with the time-lag method shows that the two sets of data are not comparable, as can be observed in Figure 7. In the time-lag measurement technique, the magnitude of the diffusion coefficient of gases in LLDPE membranes introduces some experimental problems, as we mentioned before, because the values of the time-lag parameter are reduced to only a few seconds. In this way, to

Table I Values of the Activation Energies (kJ/mol) Associated with the Permeation and Diffusion Processes of Oxygen, Carbon Dioxide, Nitrogen, and Helium in LLDPE Membranes over the Temperature Range from 298 to 348 K

	Oxygen	Carbon Dioxide	Nitrogen	Helium
E_P	29.5	22.5	33.6	32.2
E_D	28.7	30.8	27.5	35.5

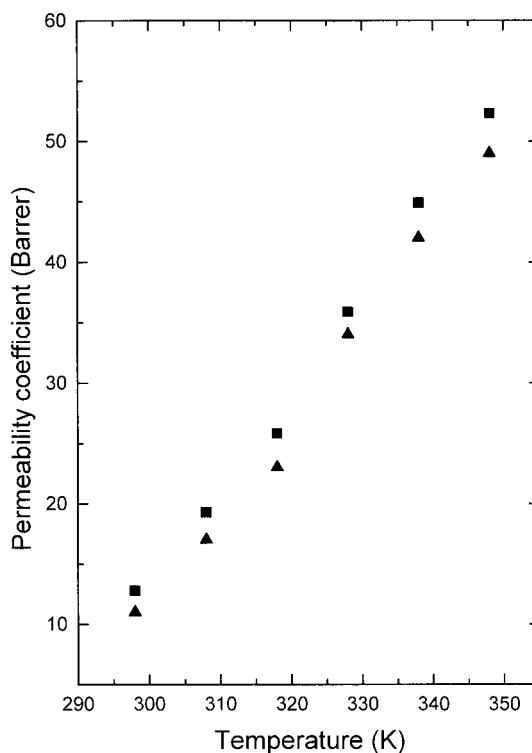


Figure 6 Comparison of the permeability coefficients of carbon dioxide in coextruded LLDPE membranes obtained by (■) Nguyen's method and (▲) the time-lag method.

increase the magnitude of the time lag and thus reduce the uncertainty of the determination of the diffusivity, we performed gas permeation measurements in LLDPE samples made up of several membranes firmly stacked together. This experimental procedure, as we discussed elsewhere,¹⁷ was apt to result in systematic errors arising mainly from the boundary effects at the interface between membranes.

Permeability coefficients for carbon dioxide and oxygen in coextruded LLDPE membranes determined by electrochemical techniques²² do not compare satisfactorily with those given for these two gases in this study. For example, the values of P for oxygen and carbon dioxide at 298 K are 1.3 and 4.5 barrer, respectively, and the values we obtained are 2.9 and 12.8 barrer, respectively. However, our diffusivity values are comparable with those reported by Compan et al.²² We obtained values of 5.1×10^{-7} and 4.9×10^{-7} cm² s⁻¹ for the diffusion coefficients of oxygen and carbon dioxide at 298 K, respectively; and the values obtained by the electrochemical technique are 3.7×10^{-7} and 5.0×10^{-7} cm² s⁻¹ for oxygen

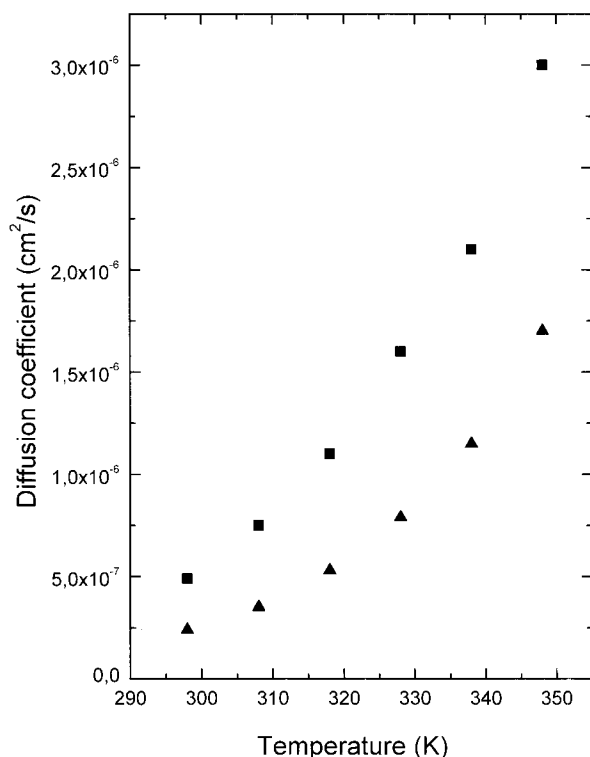


Figure 7 Comparison of the diffusion coefficients of carbon dioxide in coextruded LLDPE membranes obtained by (■) Nguyen's method and (▲) the time-lag method.

and carbon dioxide, respectively. We cannot provide an explanation for the observed discrepancy when comparing results obtained by the two techniques. Nevertheless, a comparison of data from different laboratories is difficult because the membrane history is always different and variations in test methods and inherent apparatus-induced errors are always present.

CONCLUSION

In this study, we examined the feasibility of applying an alternative permeation method for measuring the permeability and diffusivity of gases in membranes. In particular, the method was tested in coextruded LLDPE membranes, in which the estimation of the diffusivity by the time-lag method presented some problems due to both the membrane thickness and the magnitude of the diffusion coefficient. For the most part, there was good agreement between the two methods. The method employed here consistently yields slightly

higher values and seems more efficient and precise in the measurement of the diffusivity in the LLDPE membranes than the time-lag method. Moreover, the data presented in this article are comparable to data reported in the open literature for an LDPE membrane with a similar degree of crystallinity.

REFERENCES

- Barrer, R. M. *Diffusion in and through Solids*; Cambridge University Press: Cambridge, England, 1951.
- Mearns, P. *Membrane Separation Processes*; Elsevier: Amsterdam, 1976.
- Frisch, H. L.; Stern, S. A. *CRC Crit Rev Solid State Mater Sci* 1983, 11, 123.
- Stern, S. A.; Sampat, S. R.; Kulkarni, S. S. *J Polym Sci Part B: Polym Phys* 1986, 24, 2149.
- Park, G. S. In *Synthetic Membranes: Science, Engineering and Applications*; Bungay, P. M.; Lonsdale, H. K.; de Pinho, M. N., Eds.; NATO ASI Series; Reidel: Dordrecht, 1983.
- Zolanz, R. R.; Fleming, G. K. In *Membrane Handbook*; Ho, W. S. W.; Sirkar, K. K., Eds.; Chapman & Hall: New York, 1992.
- Balik, C. M. *Macromolecules* 1996, 29, 3025.
- Felder, R. M. *J Membr Sci* 1978, 3, 15.
- Koros, W. J.; Chan, A. H.; Paul, D. R. *J Membr Sci* 1977, 2, 165.
- Frisch, H. L. *J Phys Chem* 1957, 61, 93.
- Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Clarendon: Oxford, 1975.
- Paul, D. R.; DiBenedetto, A. T. *J Polym Sci Part C: Polym Symp* 1965, 10, 17.
- Jenkins, R. C. L.; Nelson, P. M.; Spier, L. *Trans Faraday Soc* 1970, 66, 1391.
- Barrie, J. M.; Spencer, H. G.; Quig, A. *Trans Faraday Soc* 1975, 71, 2459.
- Nguyen, X. Q.; Broz, Z.; Uchytel, P.; Nguyen, Q. T. *J Chem Soc Faraday Soc* 1992, 88, 3553.
- Nguyen, X. Q.; Broz, Z.; Vařák, F.; Nguyen, Q. T. *J Membr Sci* 1994, 91, 65.
- Villaluenga, J. P. G.; Seoane, B. *Eur Polym J* 2000, 36, 1697.
- Villaluenga, J. P. G.; Seoane, B. *Polymer* 1998, 39, 3955.
- Michaels, A. S.; Bixler, H. J. *J Polym Sci* 1963, 50, 413.
- Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960.
- Compañ, V.; Ribes, A.; Díaz-Calleja, R.; Riande, E. *Polymer* 1995, 36, 323.
- Compañ, V.; Ribes, A.; Díaz-Calleja, R.; Riande, E. *Polymer* 1996, 37, 2243.