

Permeability of Oxygen through Polymers. II. The Effect of Humidity and Film Thickness on the Permeation and Diffusion Coefficients

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Synopsis

The values of the permeability coefficient P (cm^2/sec) and the diffusion coefficient D (cm^2/sec), of oxygen in some water-soluble polymers at various values of relative humidity were determined. The amount of oxygen initially present in the polymer membranes was calculated. The effect of sample preparation and the film thickness on the transport parameters was investigated. The results confirm the possible effect of thickness on the rate of transport of oxygen in water-soluble polymers.

INTRODUCTION

Transport of oxygen through membranes is an important process in many industrial and biological applications. Most frequently, manometric methods are used for determining the transport of oxygen through membranes,^{1,2} but these are not easily applicable to studying hydrophilic polymers, since the physical properties of these polymers depend greatly on their water content. A polarographic method was described by Yasuda et al.³ that is more suitable for hydrophilic polymers and biological membranes.

Recently,⁴ we described a spectrophotocatalytic method for determining the permeability of oxygen through polymers. In this communication we report further work on determining the permeability coefficient P (cm^2/sec) and the diffusion coefficient D (cm^2/sec) of oxygen in hydrophilic polymers at a given relative humidity. The effect of film thickness on the transport parameters was also investigated.

EXPERIMENTAL

The flux of oxygen through membranes was measured by monitoring the sensitized photooxygenation (using polymeric Rose Bengal) of a singlet oxygen acceptor (diphenylisobenzofuran, DPBF) in a detector layer sandwiched between a support (glass) and the polymer under test. The method has been described in detail elsewhere.⁴

The samples were prepared as follows: The detector layer was prepared by coating a glass plate (microscope slide, $35 \times 26 \times 1$ mm) with a 5% solution of poly(styrene-co-benzylvinyl chloride)-supported Rose Bengal (2 ml) containing 0.01 g DPBF. Using a rotating coating table (up to approximately 1000 rpm), layers about 1–2 μm thick covering about 2 cm^2 area in the center of each slide were prepared. The glass plate with the detector layer was then overcoated with

a polymer under test. Solutions of polymers (20–30%) in water were used, and the above spinning technique was employed again.

It is well known that the physical properties of polymers depend greatly on the polymer history. This is particularly apparent for hydrophilic polymers; hence, the manner in which the samples for measuring the transport properties are prepared could affect the measured values.

Moisture sorption is especially likely to be important, and the characteristic behavior of the samples was determined by using a quartz spring balance placed in a humidity chamber. Figure 1 shows the changes in weight of a poly(N-vinylpyrrolidone) film coated on a glass support with time on changing RH (relative humidity) from 30% (CaCl₂ saturated solution) to about 58% (saturated NaBr aqueous solution). It will be seen that near equilibrium is reached within a few hours, but the sorption process continues slowly for several days. In the experiments to be described, the samples were kept for at least five days to equilibrate in a constant humidity chamber at the required RH.

A sample whose optical density was to be measured was placed into a cell equipped with two quartz windows. The atmosphere in the cell was again maintained with the appropriate saturated salt solution. The changes in the DPBF absorbance at $\lambda = 422$ nm under constant irradiation were determined. A Hilger-Watts spectrophotometer giving the optical density readings with ± 0.005 accuracy over 48 hr was used.

RESULTS AND DISCUSSION

Figure 2 shows the observed changes in DPBF concentration when the light-sensitive detector layer is irradiated under the above experimental conditions. It can be seen that the rate of disappearance of DPBF is rapid and constant in the 1.5–0.5 optical density range. The experimental data obtained in this range of optical density were used for further evaluation.

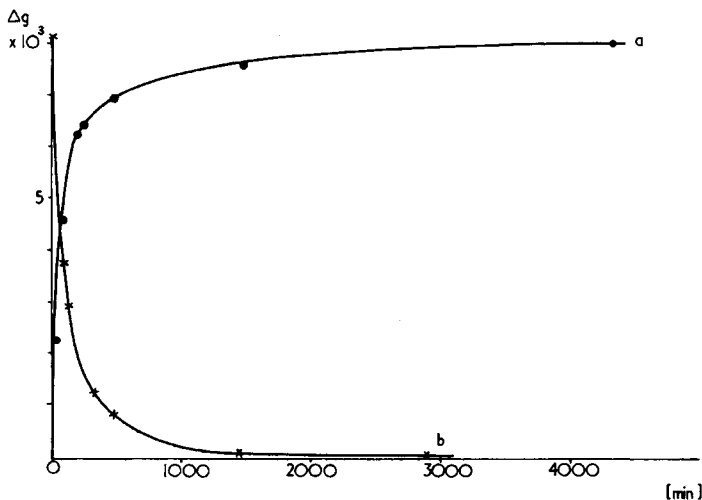


Fig. 1. Changes in weight of a poly(N-vinylpyrrolidone) sample at different values of relative humidity: (a) change of RH from 30–58%; (b) change of RH from 58–30%; sample weight at 30% RH = 0.1157 g.

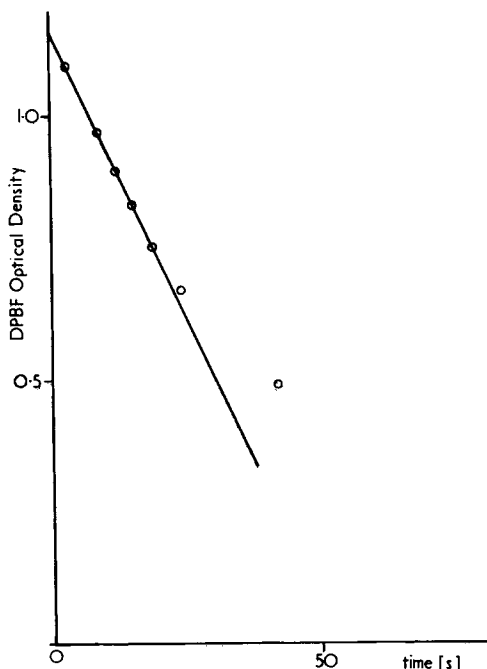


Fig. 2. Changes in DPBF optical density on irradiation of the detector layer alone.

When the detector layer is covered with a layer of polymer, the rate of disappearance of DPBF decreases and is determined by the rate of transport of oxygen through the polymer, as described previously.⁴ When the rate of DPBF disappearance approaches a steady state, the flux of oxygen through the polymer layer can be estimated and the corresponding permeation coefficient P can be evaluated.⁴ The same experimental data can be used to determine the diffusion coefficient D for oxygen in polymers.

Crank⁵ gives the amount of material diffusing in time t out of a layer of thickness l in which the initial concentration is C_1 , and the front face is maintained at this concentration, while at the rear face, (which here is in contact with the DPBF layer), the concentration is zero. The result, after a little rearrangement, is

$$\frac{Q}{lC_1} = \frac{Dt}{l^2} + \frac{1}{3} - \frac{2}{\pi^2} \sum_1^{\infty} \frac{e^{-\pi^2 n^2 Dt/l^2}}{n^2} \quad (1)$$

Thus, after a short time, the amount entering the indicator layer increases approximately linearly with time, i.e.,

$$\frac{Q}{lC_1} \rightarrow \frac{Dt}{l^2} + \frac{1}{3} \quad (2)$$

Extrapolation of this linear plot to the abscissa gives a time t_0 :

$$t_0 = -\frac{l^2}{3D} \quad (3)$$

From the experimentally determined value of t_0 , we therefore obtain the value of the diffusion coefficient D .

The experimental values of diffusion coefficient D obtained in this manner for various polymers at RH of 30% (CaCl₂ saturated aqueous solution) and 75% (NaCl saturated solution) are summarized in Table I. It can be seen that the films of hydrophilic polymers become more permeable to oxygen as the amount of water in the polymer increases.

Another quantity of interest is lC_1 , the amount of oxygen initially present in the layer. This can be derived by extrapolating the straight-line relation (2) to zero time. The intercept on the abscissa is Q/lC_1 , which is equal to $1/3$. The optical density difference (ΔOD) corresponding to this Q is obtained by extrapolation of the straight-line portion of the experimental plot and is given by

$$\Delta OD = aQ = alC_1/3 \quad (4)$$

where a is the molar absorptivity of DPBF. The concentration C_1 of oxygen in the polymer layer is then given as

$$C_1 = \frac{3(\Delta OD)}{al} \text{ (mole/liter)} \quad (5)$$

It can be seen from Table I that at the lower humidity level (RH ~30%) the solubility of oxygen in various polymers varies. The diffusion coefficient D tends to increase as the solubility of oxygen in the given polymer decreases. At the higher relative humidity (RH ~75%) the solubility of oxygen in the polymers is much lower and approaches the value of solubility of oxygen in water at equilibrium with air, saturated with water vapor at 760 mm pressure and room temperature, 2.5×10^{-4} mole/liter.⁶ A large increase in the diffusion coefficient is observed, as would be expected because of the plasticizing effect of water on hydrophilic polymers.

The permeation coefficient P is defined as

$$P = \frac{\Delta Q}{\Delta t} \frac{l}{A} (p_1 - p_2) \quad (6)$$

where ΔQ is the quantity of gas at STP that has permeated in the time interval Δt in the steady state of flow, A is the effective area of the membrane, and l is the average film thickness. The P values should be determined in the steady state of flow of penetrant. This is achieved in our experiments as indicated by the following consideration. If we take the solubility of oxygen in hydrophilic polymers to be 10^{-2} to 10^{-4} mole/liter, the total amount of oxygen in the films used in this work is of the order of 10^{-7} to 10^{-9} mole. The change in the optical density, $\Delta OD = 1$, of the detector layer of unit thickness, as caused by DPBF disappearance, requires that about 10^{-7} mole DPBF is reacted. This means that when $\Delta OD = 1$, the amount of oxygen that has passed through the film is about 1 to 10^2 times that originally present in the film. In practice, a near steady state of flow is reached when $\Delta OD = 0.1$. Previously,⁴ we established that in our case (with the assumption that the oxygen concentration at the upper surface is constant) the permeation coefficient P is given by the expression

$$P = 5.66 \times 10^{-3} \frac{\Delta OD}{\Delta t} l \quad (7)$$

Values of P are given in Table I. Also tabulated are values of the dimensionless

TABLE I
 Values of Diffusion Coefficient D , Permeation Coefficient P , Oxygen Concentration C_1 , and Solubility Parameter S for Air Oxygen in Various Water-Soluble Polymers at Room Temperature and Relative Humidity of 30 and 75%

Polymer	P , (cm ² /sec) × 10 ¹⁰	P , (cm ² /sec) × 10 ¹⁰	$S = P/D$	C_1 , (mole/liter) × 10 ⁴
		RH 30%		
Poly(N-vinylpyrrolidone) ^b	31 ± 8	9 ± 0.4	0.32 ± 0.08	33
Poly(vinylimidazole)	1.6 ± 0.6	1.3 ± 0.1	0.9 ± 0.4	220
Polyacrylamide	0.12 ± 0.05	0.46 ± 2.2	4.6 ± 2.2	380
Poly(acrylic acid) ^c	0.19 ± 0.08	0.24 ± 0.03	1.6 ± 0.7	140
Carboxymethylcellulose ^d	0.027 ± 0.008	0.10 ± 0.02	4.1 ± 1.5	390
Poly(vinyl alcohol) ^e	0.011 ± 0.002	0.06 ± 0.008	5.7 ± 1.3	540
		RH 75%		
Poly(N-vinylpyrrolidone) ^b	369 ± 70	16.8 ± 2	0.05 ± 0.01	4.0
Poly(vinylimidazole)	123 ± 12	6.2 ± 1	0.05 ± 0.01	4.0
Polyacrylamide	—	—	—	—
Poly(acrylic acid) ^c	51 ± 6	2.2 ± 0.5	0.045 ± 0.015	3.5
Carboxymethylcellulose ^d	21.6 ± 2	1.0 ± 0.2	0.05 ± 0.01	4.3
Poly(vinyl alcohol) ^e	21 ± 3	0.8 ± 0.1	0.038 ± 0.01	14.0

^a RH 30%, saturated CaCl₂ aq. solution; RH 75%, saturated NaCl aq. solution. Polyacrylamide and poly(N-vinylimidazole) were prepared by aqueous radical polymerization of the corresponding monomers.

^b BOC Ltd., K 30.

^c Borden Chem; A521668.

^d Hercules 7LF.

^e Elvanol 70-05.

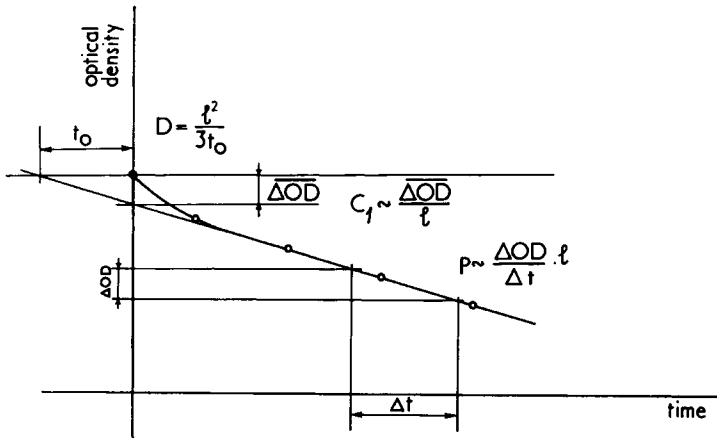


Fig. 3. Graphic evaluation of the permeation coefficient P , the diffusion coefficient D , and the initial oxygen concentration C_1 from experimental data.

ratio $P/D = S$ and the values of C_1 . The method of graphic evaluation of the experimental data is summarized in Figure 3.

On preparing the samples by drying the corresponding aqueous solutions, no significant weight changes of the samples were detected after five days of drying for the sample thicknesses used in this work. It has been noted, however, that under identical conditions, samples of different thickness may “dry” and reach apparent equilibrium but contain different relative amounts of water. With increasing thickness of the film, the relative amount of retained moisture increases. Significantly, in such cases the value of diffusion coefficient D and of permeation coefficient P were found to depend on the thickness of the measured samples (Fig. 4, Tables II and III).

The case when permeability is a function of thickness has been analyzed by Hwang and Kammermeyer.⁷ They express the total resistance to permeation in a membrane composed of two or more different layers as a sum of resistances

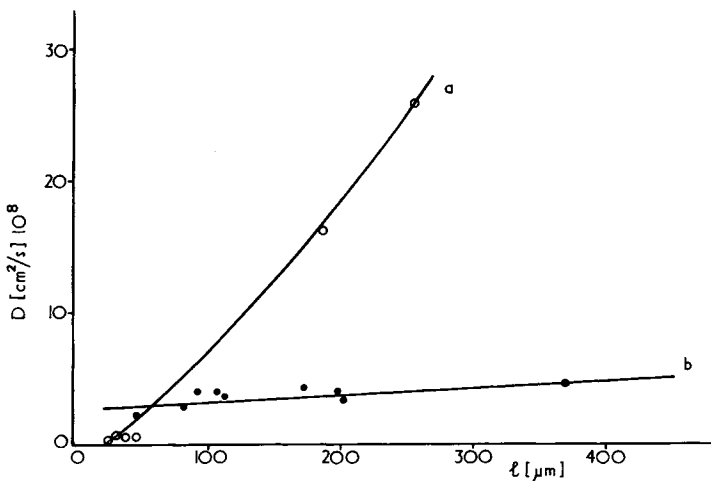


Fig. 4. Effect of film thickness on the value of diffusion coefficient D of oxygen in poly(N-vinylpyrrolidone): (a) after “drying” at 30% RH; (b) equilibrated at 75% RH.

TABLE II
Variations in D and C_1 with film thickness for Poly(N-vinylpyrrolidone) ("Drying" at ~30% RH)

$l, \mu\text{m}$	$D, (\text{cm}^2/\text{sec}) \times 10^9$	$C_1, (\text{mole/liter}) \times 10^4$
24 ± 2	2.00	46
25 ± 3	2.17	38
28 ± 2	3.11	33
34 ± 2	4.01	12
38 ± 3	5.35	12
184 ± 8	164	4.3
255 ± 8	260	3.9

of different laminates and resistances of boundary layers, and then they showed that when the membrane is heterogeneous and can be viewed as a composite laminate film, the permeability can change as a function of membrane thickness. In general, the diffusivity also becomes a function of the membrane thickness. Our results obtained with poly(vinylpyrrolidone) membranes "dried" at 30% RH indicate the presence of a rate of transport-determining layer having a critical thickness of about 200 μm . Not enough data have been collected so far to make a more accurate assessment of the critical thickness; however, the value of about 200 μm was reported previously⁷ for the critical thickness in the nylon 6-water system.

In conclusion, the results given in this communication show that our spectrophotometric method can be used to obtain the values of parameters describing the transport of oxygen in polymeric membranes at various levels of relative humidity.

The difficulties in defining the transport parameters beyond phenomenological coefficients have long been recognized.^{8,9} In addition to the known effect of temperature and pressure on permeability, our results confirm the effect of thickness on the rate of transport of oxygen in water-soluble polymers.

The results illustrate well the complex relationship between the diffusion coefficient for oxygen in hydrophilic polymers and the amount of water and dissolved oxygen in these polymers.

TABLE III
Variations of Diffusion Coefficient D and the Oxygen Concentration C_1 with Thickness of Poly(N-vinylpyrrolidone) Films^a

$l, \mu\text{m}$	$D, \text{cm}^2/\text{sec} \times 10^8$	$C_1, (\text{mole/liter}) \times 10^4$
45	2.1	9.6
80	3.0	2.6
90	4.1	3.3
105	4.1	3.2
110	3.7	4.4
170	4.3	3.5
195	3.9	1.7
200	3.4	2.3
370	4.7	1.3

^a Thickness estimated within approximately $\pm 5\%$ accuracy. The films containing a near-equilibrium amount of water ~75% RH. $D_{\text{av}} = (3.7 \pm 0.7) \times 10^{-8} \text{ cm}^2/\text{sec}$; $C_{1\text{av}} = (3.5 \pm 2.3) \times 10^{-4} \text{ mole/liter}$.

References

1. R. M. Barrer, *Diffusion In and Through Solids*, Cambridge University Press, London, 1951.
2. J. Crank and G. S. Parks, Eds., *Diffusion in Polymers*, Academic, London, New York, 1968.
3. H. Yasuda and W. Stone, Jr., *J. Polym. Sci.*, **4**, 1314 (1966).
4. K. Petrak, *J. Appl. Polymer Sci.*, **23**, 2365 (1979).
5. J. Crank, *The Mathematics of Diffusion*, Oxford University Press, London, 1975.
6. H. A. C. Montgomery, N. S. Thom, and A. Cockburn, *J. Appl. Chem.*, **14**, 280 (1964).
7. Sun-Tak Hwang and K. Kammermeyer, *Am. Chem. Soc., Div. Org. Coat. Plast. Chem. Pap.*, **34**(1), 500 (1974).
8. C. E. Rogers, J. R. Semancik, and S. Kapur, *Polym. Sci. Technol.*, **1**, 297 (1973).
9. H. Yasuda, *J. Polym. Sci. Part A-1*, **5**, 2952 (1967).

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