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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Measurement of Concentration Gradients for Diffusion of Vapors in Polymers[1,2]

BY DAVID RICHMAN AND F. A. LONG

RECEIVED JULY 29, 1959

A microradiographic technique for the determination of the concentration gradients of vapors in polymers is described. The procedure has been applied to the gradients which result from the diffusion of methyl iodide into polyvinyl acetate at temperatures above that for the glass transition. The method shows explicitly that the assumption of an equilibrium concentration at the polymer surface is valid. It also leads to diffusion coefficients which agree satisfactorily with those obtained by measurements of the rate of sorption of the methyl iodide vapor.

Introduction

Studies of the diffusion of organic vapors into polymer films using the vapor sorption technique indicate that the process is strongly dependent on the physical state of the polymer. Sorption of vapors into polymers which are at temperatures above that for the glass transition seems invariably to agree with predictions based on the assumption that the diffusion follows Fick's Law, with the further assumption that the concentration of vapor at the polymer surface is the equilibrium value for the particular pressure of vapor.[3-6] When the polymer is in the glassy state decidedly more complicated behavior frequently is observed.[4,6,7]

Since measurements of amount of vapor sorbed by a polymer film give information only on the over-all effect, it is of importance to obtain procedures which can give a more detailed picture of the diffusion process. Information on the actual concentration gradients is of particular significance and several studies of these have been made. The procedures have employed "schlieren,"[8] interferometric[9,10] and Lamm scale[11] techniques but in every case the studies actually have been for the interdiffusion of liquids and polymers and have depended on a calibration of the variation of refractive index with penetrant concentration. A procedure which is somewhat more direct and more suitable for vapor sorption was proposed by Long and Watt.[12] This involved sorption of a colored vapor with measurement of concentration gradient by a photomicrographic technique. Unfortunately, the method is severely limited by a lack of suitable colored, unreactive vapors. A modification of this method which makes use of the techniques of microradiography is the subject of the present paper.

Microradiography has found many uses in biological and industrial[13-15] problems and the general techniques are well established. In applying the method to diffusion in polymers, it is only necessary to have a penetrant whose X-ray mass absorption coefficient is markedly different from that of the polymer. The polymer is exposed to the vapor for the desired time, removed and microtomed to provide a thin cross-sectional slice of the original film. This is mounted in a fine grained photographic plate and exposed to a monochromatic X-ray beam. The exposed photographic plate is developed under standard conditions and then scanned with a microdensitometer. With

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[1] Work supported by a grant from the Office of Ordnance Research, U. S. Army.

[2] Presented in part at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

[3] S. Prager and F. A. Long, THIS JOURNAL, **73**, 4072 (1951).

[4] R. J. Kokes, F. A. Long and J. L. Hoard, *J. Chem. Phys.*, **20**, 1711 (1952).

[5] R. J. Kokes and F. A. Long, THIS JOURNAL, **75**, 6142 (1953).

[6] F. A. Long and R. J. Kokes, *ibid.*, **75**, 2232 (1953).

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[8] J. S. L. Philpot, *Nature*, **141**, 283 (1938).

[9] C. Robinson, *Proc. Roy. Soc. (London)*, **A204**, 339 (1950).

[10] J. Crank and C. Robinson, *ibid.*, **A204**, 549 (1951).

[11] A. T. Hutcheon, R. J. Kokes, J. L. Hoard and F. A. Long, *J. Chem Phys.*, **20**, 1232 (1952).

[12] F. A. Long and I. Watt, *J. Polymer Sci.*, **21**, 554 (1956).

[13] A. E. Barclay, *Brit. J. Radiology*, **20**, 394 (1947).

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[15] "Microradiography—A Bibliography," Eastman Kodak Co., Rochester, N. Y., 1955.

suitable calibration, the light transmission of the plate can give a measure of the concentration of penetrant vapor.

This method has been used to study the system methyl iodide–polyvinyl acetate at two temperatures above the glass transition temperature of the polymer. To check the validity of this new method, the same system was studied simultaneously by the vapor sorption technique and the results of the two procedures were compared.

Experimental

The sorption of methyl iodide vapor by PVA films was studied at 30 and 40° using the quartz spiral balance previously described.[3] The polyvinyl acetate was grade AYAT obtained from Carbide and Carbon Chemicals Corporation. Films were formed by casting on glass from acetone solution and were cut to a standard size of 0.96 × 2 cm. The film width, which varied with the casting but averaged 0.020 cm., was determined with a micrometer. The cut film was suspended from the quartz spiral balance in an evacuated chamber and at time zero a predetermined pressure of methyl iodide vapor (200 mm. at 40° and 138 mm. at 30°, both values of which lead to a relative pressure, P/P_0, of 0.285) was admitted to the chamber. The increase in length of the spiral as a function of time was followed with a cathetometer. For an experiment solely on sorption the vapor takeup was followed until there was no change in spring length for at least 18 hr. If the sample was to be removed for X-ray examination, the sorption was followed until the predetermined time for removal. The chamber was rapidly filled with air and the sample removed and quenched in liquid nitrogen. The film then was trimmed to expose a cross section well distant from any edge of the film and mounted in the microtome with the freshly exposed surface over the cutting blade. The orientation was such that the blade ran parallel to the newly exposed surface.

The microtome used in this study was a standard Spencer machine which could be set to make cuts with widths of from two microns up. The microtome blade was a carefully sharpened Schick razor blade. Unless the blades were specially prepared the sliced films had surface striations which gave unsatisfactory results. The preparation of the razor blade to give a suitable cutting edge required three stages of polishing as recommended by Hellier.[16] For the successive stages the abrasives used were levigated alumina, Linde A5175 and finally Linde B5125. The progress of the polishing was monitored by frequent examination under a microscope.

The samples obtained from the microtoming were mounted in a specially designed X-ray camera and exposed to radiation. The camera consisted of a body of the type described by Sherwood[17] modified to hold a 1″ × 3″ photographic plate and with a brass face plate which bolted to the body. This face plate acted as the mount for a cellophane diaphragm which served as the flexible membrane discussed by Sherwood. There were three entrance ports drilled in the face plate so that each photographic plate could be used for three exposures. Provision was made for a collimator to be attached to the outside of the face-plate and this was used to align the camera ports with the X-ray beam. The microtome slices were mounted on the cellophane diaphragm with a dab of Duco cement. They were oriented so that the X-ray beam would pass through the slice perpendicular to the direction of diffusion.

When the face plate was bolted into position, the polymer samples were sandwiched between the diaphragm and the photographic plate. During the exposure period the camera was evacuated. This maintained a pressure differential on the two sides of the diaphragm and ensured close contact between the polymer slices and the photographic plate. This procedure is especially important in maintaining an adequately sharp image.

To prevent visible light from entering the camera, the outside of the entrance ports was covered with one mil aluminum foil. Densitometer traces of sample blanks indicated that the aluminum, cellophane combination did not affect the uniformity of the X-ray beam incident on the photographic plate.

The X-ray source used for this work was a standard Norelco diffraction machine equipped with a chromium tube. The camera was mounted about six inches from the X-ray source and the unfiltered X-ray beam was used. The photographic plates were made of Kodak emulsion 548-0 spread on 1″ × 3″ glass plates. To harden the emulsion before using, the plates were dried over Drierite in a desiccator for 1 hr. The four minute exposure to the X-ray beam was followed by a five minute development in Kodak 0-19 with constant brushing.

The transmission of the exposed photographic plates was determined with a microdensitometer.[18] The machine used projected an enlarged image of the photographic plate on to an adjustable slit in front of a photomultiplier tube. The output of the tube was recorded on a strip chart after suitable amplification. An effective slit width of 6 × 10⁻⁴ cm. was obtainable by using a very narrow physical slit with high magnification objectives in the projection system. The electronics were such that the per cent. of light transmitted was recorded directly. The intensity required for full scale deflection and the reference to be used as zero transmission could also be set by manual adjustment. In this work the zero transmission level was taken to be the background of the exposed photographic plate. This allowed the transmission ratio for two regions of the photographic plate to be determined directly from the pen deflection ratio of the densitometer trace. The photographic plates were scanned by passing them under the projection lens on a bed driven by a constant speed motor. The rate at which the plate moved when combined with the chart speed gave the conversion factor for calculation of distance on the photographic plate from divisions on the chart paper.

Two other pieces of experimental information are necessary to calculate the concentration distance curve from the densitometer trace. One is the thickness of the sample through which the X-ray beam passed. The other is the gamma value for the photographic plate. The film thickness was measured with a microscope equipped with a calibrated micrometer eye piece. The gamma value of the film was determined by two methods, one of which was to vary the exposure time and find the optical density of the plate as a function of the exposure time. The second method was to photograph simultaneously a group of polymer strips of various thicknesses and with known mass absorption coefficients and to calculate gamma from the observed transmission ratios.

The calculation of concentration–distance curves from the densitometer traces is based upon the following considerations. If an X-ray beam is passed through a medium of thickness x then the intensity of the emergent beam I is related to the incident intensity I_0 by

$$I = I_0e^{-M\rho x} \qquad (1)$$

where M is the mass absorption coefficient for the medium and ρ its density. The mass absorption coefficient for a compound may be found by taking the product of the weight fractions of the elements times the atomic mass absorption coefficients and summing over the elements in the compound. Since the mass absorption coefficient of the sample is a function of X-ray wave length, a monochromatic X-ray beam is used. For PVA the mass absorption coefficient based on the repeating unit in the chain was found to be 25. A similar calculation for methyl iodide gave a mass absorption coefficient of 725. The mass absorption coefficient of a polymer containing α grams of vapor per gram of polymer is given by

$$M_p\frac{1}{1+\alpha} + M_v\frac{\alpha}{1+\alpha} \qquad (2)$$

where subscripts p and v stand for polymer and vapor, respectively. If additivity of volumes is assumed then the density of the sample is given by

$$\frac{(1+\alpha)\rho_p\rho_v}{\rho_v + \alpha\rho_p} \qquad (3)$$

where the density of the sorbed vapor is taken to be its liquid density.

The transmission T of a photographic plate is related to the exposure It where t is the time and I the incident in-

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(16) J. Hellier, *Rev. Sci. Instr.*, **22**, 185 (1951).

(17) H. F. Sherwood, *ibid.*, **18**, 80 (1947).

(18) We are indebted to the Physics Department of Cornell University for the use of their specially constructed microdensitometer.

tensity by

$$\log \frac{1}{T} = \gamma \log It \qquad (4)$$

When two regions of the same photographic plates are compared

$$\log \frac{T_1}{T_2} = \gamma \log I_2/I_1 \qquad (5)$$

Now let T_1 represent the plate region corresponding to a polymer containing vapor and T_2 to a region from a reference of the same thickness x then it follows from the above that the concentration of vapor is given by

$$\alpha = \frac{(M_\mathrm{p})\rho_\mathrm{p}\rho_\mathrm{v}\, x - \rho_\mathrm{v}\left[\dfrac{\log \dfrac{T_1}{T_2}}{\gamma} + (M_\mathrm{R})\, \rho_\mathrm{R}\, x\right]}{\rho_\mathrm{p}\left[\dfrac{\log T_1/T_2}{\gamma} + (M_\mathrm{R})\, \rho_\mathrm{R}\, x\right] - (M_\mathrm{v})\, \rho_\mathrm{v}\, \rho_\mathrm{p}\, x} \qquad (6)$$

where the subscript R stands for the reference material. When R is the pure polymer this reduces to

$$\alpha = -\rho_\mathrm{v}\frac{\log T_1/T_2}{\gamma}$$
$$\left[-(M_\mathrm{v})\, \rho_\mathrm{v}\rho_\mathrm{p}\, x + \rho_\mathrm{p}\frac{\log T_1/T_2}{\gamma} + (M_\mathrm{p})\, \rho_\mathrm{p}^2\, x\right] \qquad (7)$$

Calculations.—The appropriate form of Fick's law for sorption in polymers is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D\left(\frac{\partial c}{\partial x}\right)\right] \qquad (8)$$

where D is the diffusion coefficient and c is the concentration of penetrant at time t at a distance x from the film surface. For sorption into a film of non-glassy polymer, the boundary conditions are assumed to be

$$c(0,t) = c(l,t) = c_\mathrm{eq}$$
$$c(x,0) = c_\mathrm{i}$$

where c_i and c_eq are the initial and final equilibrium concentrations of vapor in the polymer and l is film width.

It is found for most polymer-penetrant systems that the diffusion coefficient is an exponential function of the concentration[3-6] and under this condition the diffusion equation cannot be solved in analytic form. However, Crank and Park[19] have shown that the integral diffusion coefficient defined as

$$\bar{D} = \frac{1}{c_\mathrm{eq} - c_\mathrm{i}}\int_{c_\mathrm{i}}^{c_\mathrm{eq}} D(c)\, \mathrm{d}c \qquad (9)$$

can be well approximated by

$$\bar{D} = \frac{\pi}{32}\left[K_\mathrm{S}^2 + K_\mathrm{D}^2\right] \qquad (10)$$

where K_s is the slope of the sorption curve plotted as Q_t/Q_∞ *vs.* $\sqrt{t}/l$ where Q_t is the amount of vapor sorbed at time t and Q_∞ is the equilibrium amount of vapor sorbed and where K_D is the corresponding desorption slope. An upper estimate to $\bar{D}$ is given by

$$\bar{D} = \frac{\pi}{16}K_\mathrm{S}^2$$

since for Fickian diffusion K_S is always equal to or greater than K_D.[20]

To calculate diffusion coefficients from a concentration–distance curve the relation used is[21]

$$D_{c = c_\mathrm{i}} = -\frac{1}{2t}\left(\frac{\mathrm{d}x}{\mathrm{d}c}\right)_{c = c_\mathrm{i}}\int_0^{c_\mathrm{i}} x\, \mathrm{d}c$$

where $(\mathrm{d}c/\mathrm{d}x)_{c = c_\mathrm{i}}$ is the slope of the curve at the concentration of interest and the integral is the area under the curve up to that concentration. By calculating D for several concentrations the functional dependence of D on c can be determined. To compare these diffusion coefficients with those from sorption studies it is necessary to employ the functional dependence implied by the definition of the integral diffusion coefficient. Experimentally the diffusion coefficient is usually related to the concentration c by an exponential equation of the form

$$D(c) = D_0 e^{\beta c} \qquad (11)$$

Inserting this into eq. 9 leads to

$$\bar{D} = \frac{D_0}{c_\mathrm{eq}\beta}\left[e^{\beta c_\mathrm{eq}} - 1\right] \qquad (12)$$

where c_i is taken as zero for an initially dry film of polymer.

Results and Discussion

The results of a typical sorption experiment for methyl iodide into PVA at 40° are shown in Fig. 1. The initial linear behavior and the approach to a final equilibrium indicate that the diffusion is indeed Fickian. Figure 2 shows the initial slopes for sorption runs at 30 and 40°. These curves terminate at the point at which the film was removed for the X-ray analysis. From the slopes, the measured film thicknesses and the equilibrium concentrations, the integral diffusion coefficients were obtained. These were found to be 4.3×10^{-9} cm.²/min. at 30° and 2.4×10^{-8} cm.²/min. at 40°. Since the vapor activity was chosen to be the same at the two temperatures, these values can be used to obtain an estimate of the activation energy for the diffusion process. This was found to be 33 kcal. per mole, a figure which is in rough agreement with the value obtained for acetone diffusing into PVA at the same temperatures.[4]

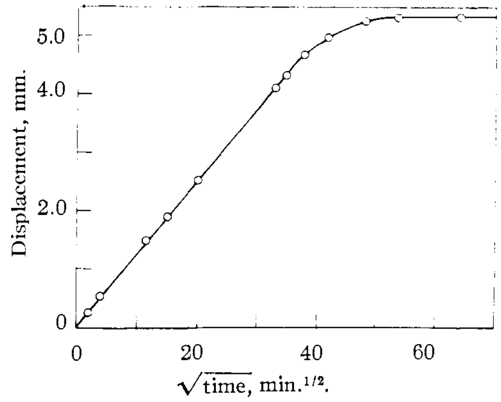

Fig. 1.—Sorption of 200 mm. of methyl iodide vapor into polyvinyl acetate at 40°. Film width is 1.8×10^{-2} cm.

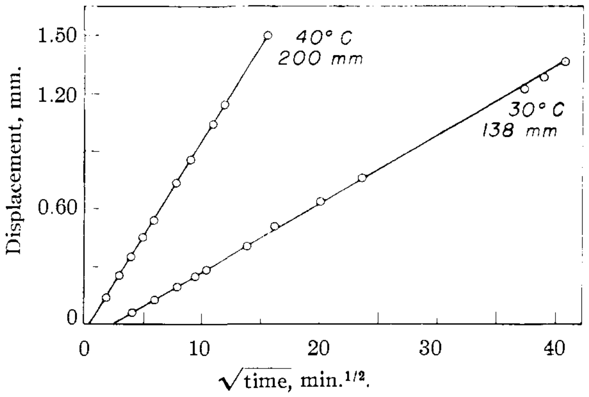

Fig. 2.—Initial stages of sorption of methyl iodide at an activity of 0.285 into films of PVA. Film widths are 2.3×10^{-2} cm.

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(19) J. Crank and G. S. Park, *Trans. Faraday Soc.*, **45**, 240 (1949).

(20) J. Crank, "Mathematics of Diffusion," Oxford Press, London, p. 242 and Chapter 12.

(21) Ref. 20, p. 232.

Typical densitometer traces for three different times of sorption of methyl iodide in PVA at 30° are shown in Fig. 3. The total sorption for these systems varies from about 9% of the final equilibrium for that of Fig. 3c to 20% for 3a. The two peaks in these traces correspond to the regions in which the polymers contain penetrant. The plateau between the peaks indicates a region of pure polymer as yet free of penetrant.[22] In principle the outer edges of these traces should be vertical (corresponding to the physical edges of the slices). That they are not entirely vertical is partly due to the finite size of the slit opening of the densitometer and perhaps partly due to lack of vertical alignment of the sample with the X-ray beam. The fact that the slices are measurably thick (normally 80 μ) also leads to a small contribution to the "blurriness." The rounding of the outside of the peak top is most probably due to diffusion of vapor back out of the sample between the time it is removed from the sorption apparatus and the time it is quenched in liquid nitrogen. This rounding is much more evident in the runs at 40°, a fact which is consistent with the larger diffusion coefficient at the higher temperatures. These various effects made it difficult to establish the exact point which corresponds to the edge of the polymer film. In practice the edge was taken to be the point of the half-height of the peak in the densitometer trace. Film widths calculated in this manner actually agreed quite well with the widths determined with a micrometer before the run was started.

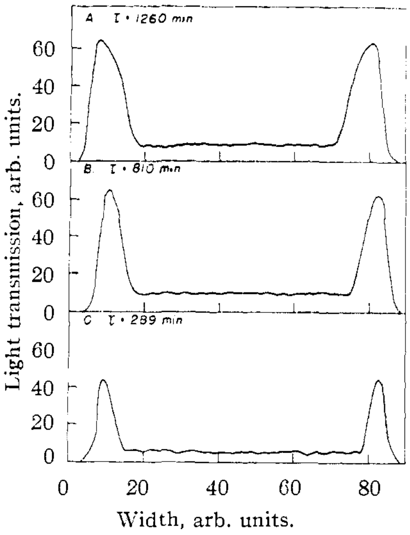

Fig. 3.—Densitometer traces for microtomed slices of PVA after exposure to 138 mm. of methyl iodide vapor for stated times at 30°. Slice thicknesses are roughly 80 μ: film widths are in the order of 2.3 × 10^{-2} cm.

Figure 4 gives the concentration distance curves which have been calculated from the densitometer traces. The curves shown in this figure are averages obtained from several densitometer traces taken for each of the three times of 289, 810 and 1260 minutes, those in Fig. 3 being representative. The vertical lines in Fig. 4a indicate the type of scatter found for the repeat runs.

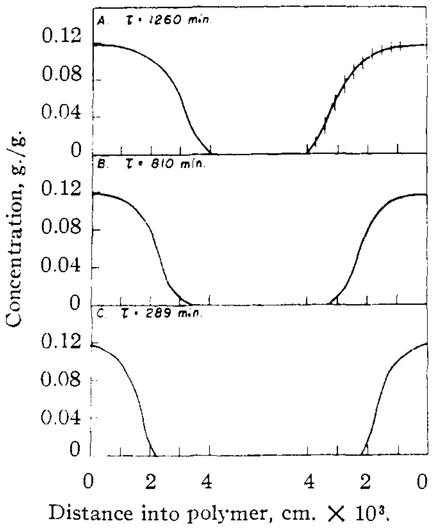

Fig. 4.—Averaged concentration–distance curves for diffusion of 138 mm. of methyl iodide into PVA at 30°.

Two preliminary comparisons of Fig. 4 with the data from conventional sorption experiments can be made. As noted earlier, the normally assumed boundary condition for sorption with Fickian diffusion is that the concentration of penetrant at the polymer surface is at all times the equilibrium value. It is of interest then that the three sets of curves of Fig. 4 indicate a virtually constant surface concentration of 0.12 g./g., a value which agrees well with the observed equilibrium sorption value of 0.13 g./g. for methyl iodide at the given pressure and temperature. Another comparison involves the total sorption as indicated by the areas under the curves. Examination of the curves in Fig. 4 shows that the ratio of the area under the 810 min. curve to that under the 289 min. curve is 1.3 and the similar ratio of the 1260 min. curve to the 810 min. curve is 1.5. The vapor sorption experiments which were terminated at these same times gave the corresponding ratios of weight gain as 1.3 and 1.7.

Diffusion coefficients were calculated from the concentration distance curve of Fig. 4a for five values of the penetrant concentration. A similar calculation was done for an equivalent run at 40°. The results are shown in Fig. 5 which gives the calculated diffusion coefficients as a function of the concentration. The slopes and intercepts of the curves give values of the parameters β and D_0 of eq. 11. These then were used to calculate integral diffusion coefficients for the two temperatures. The resulting values of $\overline{D}$ in units of cm.^{2}/min. are 2.1 × 10^{-9} at 30° and 1.2 × 10^{-8} at 40°, both for a final concentration of 0.12 g./g. These are to be compared to the values of 4.3 × 10^{-9} and 2.4 × 10^{-8} obtained from conventional sorption experiments. Remembering that values of $\overline{D}$ from sorption alone are in reality upper limits which may be too large by as much as a

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(22) The "twin-peaked" character of the densitometer traces for methyl iodide–PVA is maintained up to relatively high degrees of sorption. Thus the trace for a slice of a film of original width 2.3 × 10^{-2} cm. and containing over 50% of the equilibrium sorption still shows separated peaks indicating that the center of the film has not been penetrated by the vapor. As will be shown later the situation or polymers which are in the glassy state is very different.

factor of two, the quantitative agreement between the two procedures is quite satisfactory.

These comparisons indicate that the microradiographic technique is capable of following the process of diffusion of organic molecules in polymers and that the results obtained are in good agreement with those obtained by more standard methods of investigation. The method is experimentally fairly simple and has the virtue of giving direct information about the concentration gradients. In the present study the accuracy is not very high, probably lower than for the vapor sorption method. However, many of the details of the procedures could be improved with a consequent increase in accuracy. As one example, the conventional microtome is not a very good instrument for getting smooth, well-aligned slices of polymeric materials. An improvement here could both improve the accuracy and broaden the applicability of the method since at present the greatly softened polymer samples which result from extensive sorption are almost impossible to slice satisfactorily. It would also improve the procedure if reference slices of material of known thickness and absorption coefficient were included in all photographs. These could serve as internal standards and minimize errors due to variations in film, developing procedures, etc. In spite of these last comments the method in its present state is capable of following the diffusion process with an accuracy which is adequate for many purposes. It should be of particular use in situations where the diffusion is experimentally complex. The paper which follows illustrates this for the complicated case of sorption of vapors into glassy polymers.

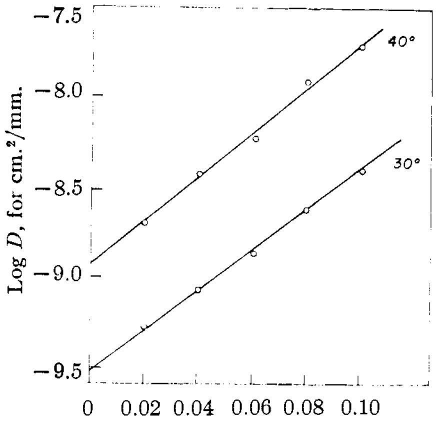

Fig. 5.—Diffusion coefficients calculated from concentration–distance curves for methyl iodide in PVA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Concentration Gradients for Diffusion of Vapors in Glassy Polymers and their Relation to Time Dependent Diffusion Phenomena[1,2]

BY F. A. LONG AND DAVID RICHMAN

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Conventional weight gain experiments have been made for the sorption of methyl iodide vapor into films of polyvinyl acetate at 20° and also into films of cellulose acetate at 40°. Both systems exhibit the characteristic "anomalous" behavior which normally accompanies diffusion of organic vapors into glassy polymers. The concentration gradients which result from this diffusion have been measured for these systems using the microradiographic procedure. The observed gradients are very different from those found for diffusion into non-glassy polymers. In particular the surface concentrations attain their equilibrium values only very slowly, varying with time according to the equation $C_s = C_0 + (C_{eq} - C_0)[1 - \exp(-\beta t)]$. The initial surface concentration C_0 is commonly only a small fraction of the final value C_{eq}. If one now assumes this dependence of surface concentration on time and also utilizes a constant value for the diffusion coefficient, it is possible to obtain explicit solutions for Fick's Law for diffusion both into an initially dry polymer and into a polymer preëquilibrated with a given amount of the vapor. The resulting equations can explain the anomalous behavior found for the former case and the two-stage behavior found for the latter.

Introduction

It is now well established that diffusion of vapors into polymers which are in the glassy state is frequently quite different than that for polymers which are at temperatures above that for their glass transition. For the latter situation the diffusion seems invariably to obey Fick's Law with the usual boundary condition that the concentration at the polymer surface is the equilibrium value for the particular pressure of vapor. If the concentration of vapor is very low, Fick's Law seems to be obeyed with glassy polymers also but the temperature coefficients are quite different from those found for non-glassy materials.[3–5] However, when the vapor concentrations are relatively high, diffusion into glassy polymers is often anomalous or non-Fickian in the sense that Fick's Law with the usual boundary conditions is not obeyed.[6–15] These differences are especially striking when the dif-

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[1] Work supported by a grant from the Office of Ordnance Research, U. S. Army.

[2] Presented in part at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

[3] P. Meares, THIS JOURNAL, **76**, 3415 (1954).

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