

Diffusion of Liquids in Cellulose Membranes

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Synopsis

Diffusion of small quantities of liquids in porous polymeric substrates has been studied by means of a radiotracer technique. The procedure has been applied to the permeation of five different types of paper stock by ethylene-1,2- C^{14} glycol. Data obtained indicate that under the experimental conditions the diffusion analogy is valid for solvent penetration in the systems studied. The method should have general applicability to studies of diffusion rates in cellulosic and other membranes and to investigations where only small quantities of diffusant are available.

INTRODUCTION

Diffusion of liquids into porous substrates like cellulose has been studied extensively.¹⁻⁵ In most cases, however, owing partly to experimental difficulties, data are available only on transport of relatively large quantities of nonvolatile liquids, and considerable time has often elapsed between application of diffusant to substrate and the first measurement of depth of penetration. We wish to report results on the kinetics of diffusion and flow characteristics through different types of paper surfaces by means of a radioactive tracer technique.

The method of investigation consisted of applying a thin film of C^{14} -labeled solution to the porous substrate and measuring the change in radioactive counts with time. This procedure is not limited to large volumes of liquids of low vapor pressure; the only restriction is that the rate of evaporation of the liquid from the substrate surface must be less than its rate of penetration.

Depending on the method of application of diffusant to substrate, a viscosity of 1 poise or more may be desirable. This presents no difficulty, since a chemically inert solute may be dissolved in the penetrant to increase its viscosity. Rudd⁶ has recently given a mathematical analysis of the paper adsorption chromatographic phenomenon in which he demonstrated that solvent and solute penetration may be treated independently. Experimental confirmation of this has also been established in our laboratory.⁷ With C^{14} -labeled ethylene glycol, the rate of its diffusion was found equal to that of a C^{14} -labeled ethylene glycol solution of abietic acid with a viscosity of ca. 70 poise.

EQUATIONS FOR DIFFUSIVE FLOW

For the specific case of one-dimensional diffusion, where the total amount of material remains constant and is placed on the surface (at the plane $x = 0$) of a semi-infinite solid and left to diffuse into it, Barrer⁸ has given the solution of Fick's law as

$$C(x,t) = [Q/(\pi Dt)^{1/2}] \exp \{ -x^2/4Dt \} \quad (1)$$

where $C(x,t)$ is the concentration of diffusing material after a diffusion time t at a penetration depth x from the surface, Q is the total amount of diffusant, and D is the diffusion coefficient.

At the plane $x = 0$, eq. (1) reduces to

$$C(x = 0) = Q/(\pi Dt)^{1/2} \quad (2)$$

giving the change in concentration of diffusing molecules with time at the surface. To satisfy the boundary conditions of eq. (1), the rate of evaporation of the radioactive material must be minimized and less than the rate of diffusion.

EXPERIMENTAL

Circular disks were cut from two types of filter paper (Whatman No. 3MM and No. 1), two kinds of kraft stock (natural and bleached), and one coated stock, affixed to aluminum planchets to provide a flat surface, and conditioned at ca. 10% R.H. for at least 48 hr. Specimens were coated with a 0.46% solution of abietic acid (Matheson, Coleman and Bell) in ethylene glycol (Eastman White Label) to which 0.12 mcuries of ethylene-1,2-C¹⁴ glycol (New England Nuclear Corp.) had been added. A uniform deposition of solution with average thickness of 0.2–0.3 mg./cm.² (2600 cpm./mg.) resulted from this technique.

After the radioactive solution had been applied to each disk, the disk was placed immediately in the counter, and the decrease in the number of surface counts (self-absorption) with time was recorded. The method of Yankwich and Weigl⁹ was used to calculate depth of penetration from self-absorption data.

The radioactivity of each disk was measured with a thin-window flow counter. A conventional commercial rate meter and recorder were used. The counter was enclosed in a constant humidity chamber maintained at an ambient relative humidity of ca. 10% at all times. All operations were carried out at constant humidity to prevent changes in the physical properties of cellulose due to changes in ambient conditions.

RESULTS

Typical experimental results are plotted in Figure 1, where decrease in surface concentration of ethylene glycol is plotted against time for the Whatman 3MM system. Values were readily reproduced for each sub-

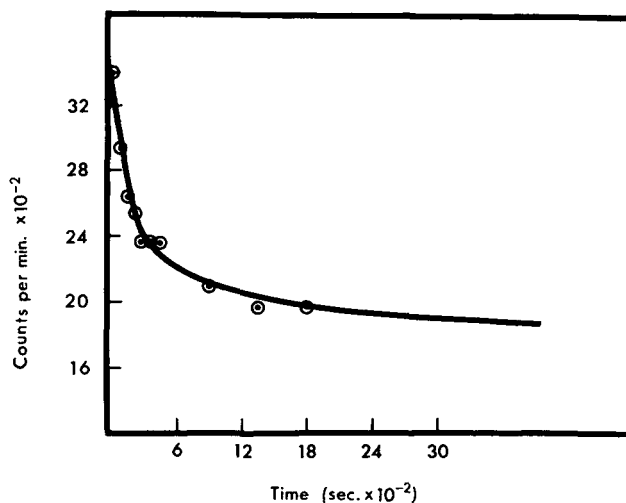


Fig. 1. Concentration profile for sorption of ethylene glycol by Whatman No. 3MM.

strate investigated when sheet-to-sheet variations were taken into consideration.

The square of the penetration depth was plotted against time for five different paper substrates to obtain the flow-rate profile shown in Figure 2. It is noteworthy that a linear relation was found in the early stages of sorption, indicating Fickian diffusion with a constant diffusion coefficient. The Boltzmann relation, linearity of penetration depth with $(\text{time})^{1/2}$ at a given concentration, serves as a means of correcting for the effective initial time in free diffusion.

The slopes of these curves afford flow rate coefficients k that should be constant with time.¹⁰ Because diffusion is a structure-dependent process, flow rate coefficients can vary with such properties as porosity, surface energy, and elasticity of the substrate, as shown in Table I. For example,

TABLE I
Penetration of Paper Substrates by Ethylene-1,2-C¹⁴ Glycol

Sample	Flow rate coefficient k , cm. ² /sec. $\times 10^9$	Diffusion coefficient D , cm. ² /sec. $\times 10^{10}$
Whatman No. 3MM	21.1	94.4
Whatman No. 1	10.1	32.8
Bleached kraft	4.2	15.9
Natural kraft	1.2	4.0
Coated stock	0.24	0.78

Whatman No. 3MM and Whatman No. 1, extremely porous, pure cellulosic materials, have flow rate coefficients of 21.1×10^{-9} and 10.1×10^{-9} cm.²/sec., respectively, as compared with natural and bleached kraft

stocks of low porosity, low degree of fibrillation, containing rosin and mineral filler with $k = 1.20 \times 10^{-9}$ and 4.2×10^{-9} cm.²/sec., respectively. Electron micrographs of representative areas from each stock are shown in Figure 3. With super-calendered paper, Hsu³ obtained a flow rate coefficient of 9×10^{-9} cm.²/sec. for a colloiddally dispersed resin system in which the dispersed phase separated from the dispersion medium during diffusion.

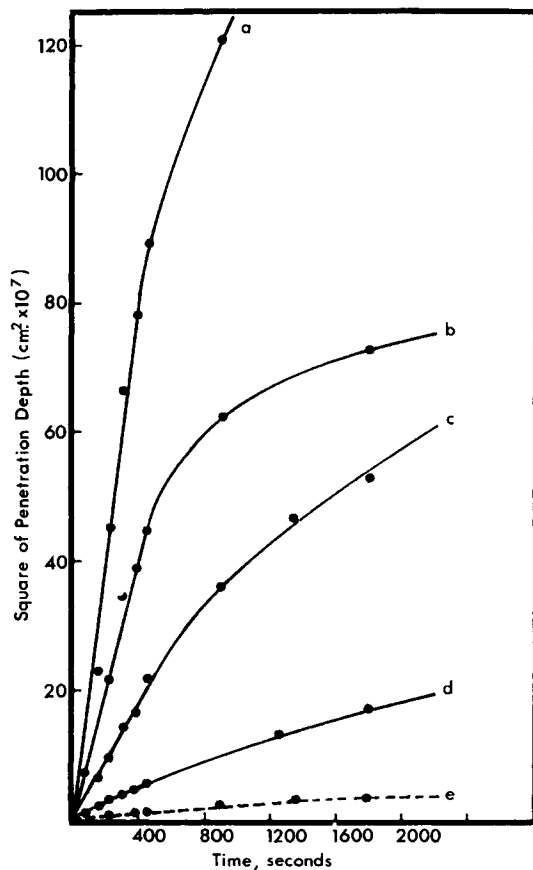


Fig. 2. Rate of sorption of ethylene glycol by five substrates: (a) Whatman No. 3 MM; (b) Whatman No. 1; (c) bleached kraft; (d) natural kraft; (e) coated stock.

In contrast, when ethylene glycol was applied to a starch-latex dispersion of TiO_2 -clay coated on a cellulose base, the flow rate coefficient decreased to 0.24×10^{-9} cm.²/sec. (Fig. 2). Since electron micrographs (Fig. 3) revealed that the coating provided a continuous surface over the fibrous structure of the substrate, differences in k can be attributed only to the decreased penetrability of a TiO_2 -clay-latex dispersion as contrasted with that of cellulose.

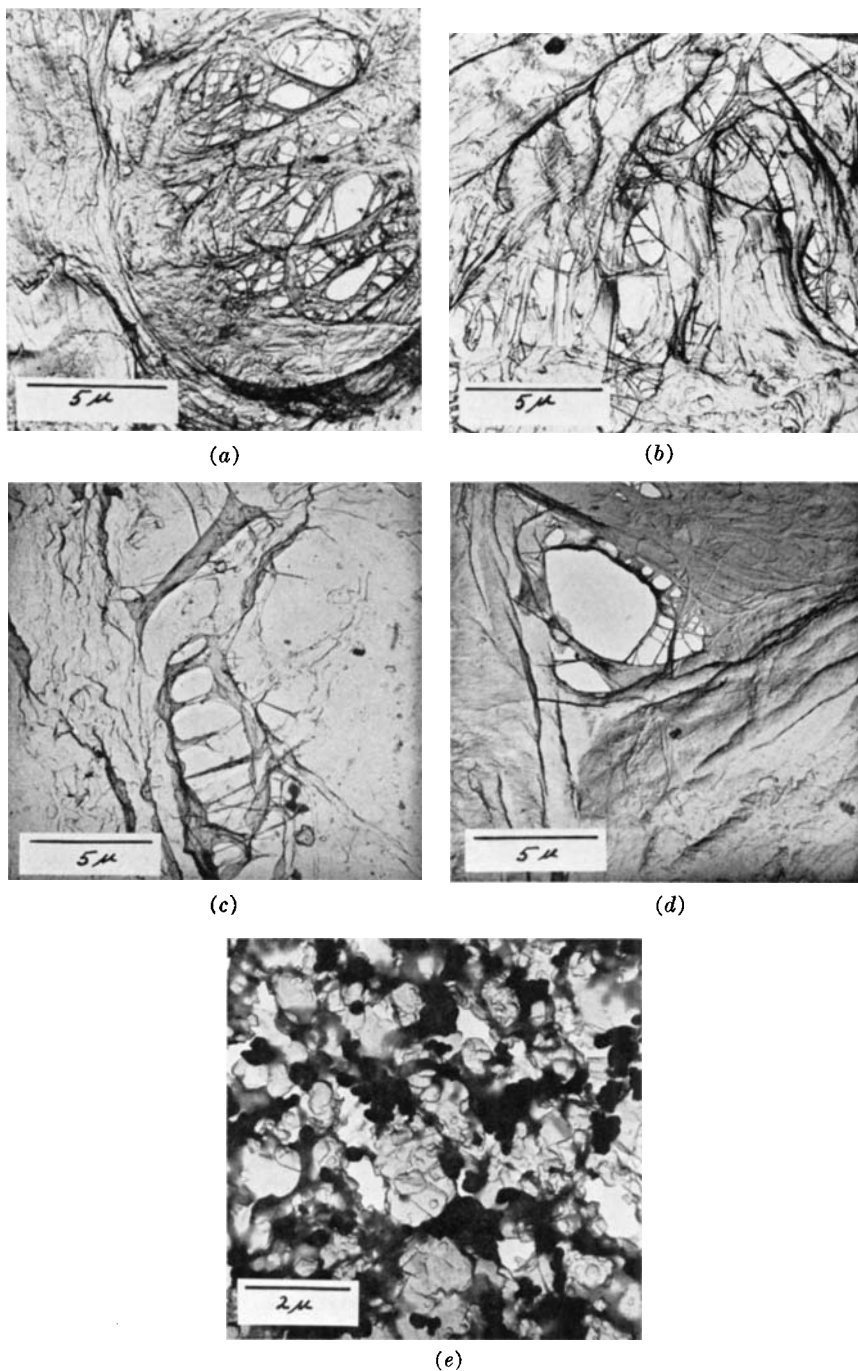


Fig. 3. Electron micrographs, palladium-shadowed carbon replicas showing relative porosities of paper substrates: (a) Whatman No. 3MM; (b) Whatman No. 1; (c) bleached kraft; (d) natural kraft; (e) coated stock, TiO_2 -clay-latex.

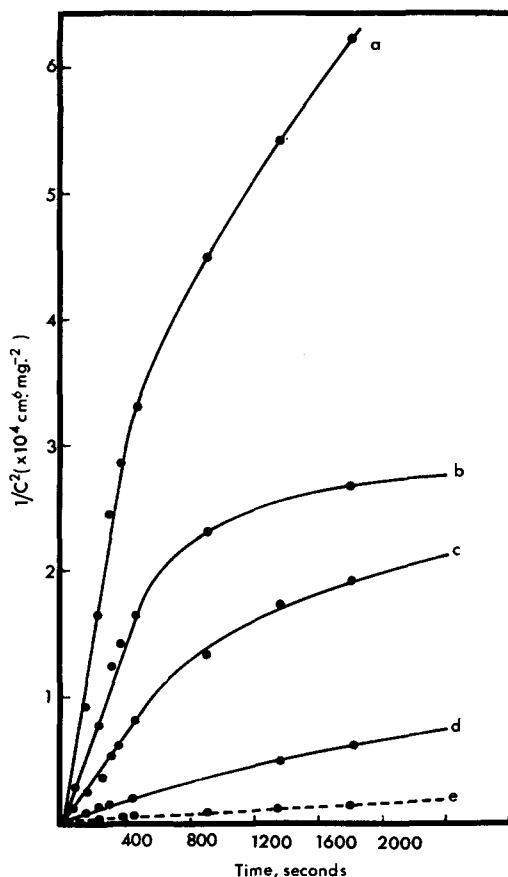


Fig. 4. Surface concentration of ethylene glycol as a function of time: (a) Whatman No. 3MM; (b) Whatman No. 1; (c) bleached kraft; (d) natural kraft; (e) coated stock.

By using the data from Figure 2, the change in surface concentration of ethylene glycol was obtained and plotted as a function of time (Fig. 4). Diffusion coefficients were calculated from the slope according to the relation given in eq. (2). Diffusivities of ethylene glycol as a function of the nature of the cellulose substrate at 25°C. and 10% R.H. are given in Table I.

DISCUSSION

Diffusion in Cellulose

Transport of ethylene glycol through cellulose may be interpreted as either diffusive or viscous flow.¹¹ In viscous flow, molecules of the penetrant are considered to move as groups through the substrate, whereas in diffusion, molecules of the penetrant are assumed to move singly in a

random manner. In this system, both processes result in the net transfer of matter from a region of higher to one of lower concentration.

From Ticknor's concept,¹¹ it is possible to determine whether the movement of ethylene glycol through a paper substrate is either diffusion-controlled or a viscous-flow process. In a viscous process, the rate of transport would be expected to be much larger than that for diffusion. In the former, penetrant molecules are moving in groups; in the latter, molecules are moving singly.

Diffusion may be interpreted (Eyring concept) as the movement of diffusing molecules from hole to hole in the amorphous regions of the cellulose polymer; cellulose can be considered as a mass of polymer chains and holes, with the holes forming and disappearing as a result of segmental motion of the polymer. Thus, comparing the rate of diffusion as calculated from Fick's law [eq. (2)] with the self-diffusion coefficient of ethylene glycol (where diffusion is the only process) should distinguish between a viscous flow and a diffusion mechanism of penetration. The self-diffusion coefficient of ethylene glycol would represent the limiting value for the diffusion coefficient.

Using the Stokes-Einstein equation

$$D = RT/6\pi N\eta r \quad (3)$$

the self-diffusion coefficient D for ethylene glycol is calculated to be 4.1×10^{-7} cm.²/sec. Since $D\eta$ (at constant temperature) is a constant, to compare this result with our data, we have multiplied all diffusion coefficients by the viscosity. These data are given in Table II.

TABLE II
Diffusion Coefficients of Ethylene-1,2-C¹⁴ Glycol through Paper
Substrates at 25°C.

Sample	$D\eta$, poise-cm. ² /sec. $\times 10^9$
Ethylene-1,2-C ¹⁴ glycol	70
Whatman No. 3MM	1.6
Whatman No. 1	0.57
Bleached kraft	0.28
Natural kraft	0.069
Coated stock	0.014

The observed diffusion coefficients in Table II for these systems are from one to three orders of magnitude less than the self-diffusion coefficient for ethylene glycol calculated from the Stokes-Einstein equation. It appears, therefore, from these data that diffusive rather than viscous flow is the major transport mechanism through cellulose substrates of this type.

The process of diffusion in noncoherent cellulose membranes of paper is governed by the capillary nature of the substance, i.e., the type and size

of the pore system. These properties, in turn, are functions of the molecular structure of the paper substrate that determines segmental mobility and therefore diffusion rate.

From Table II, it can be seen that the diffusivity varies by about two orders of magnitude for uncoated papers. This sensitivity of diffusion coefficient to the microstructure of the substrate also suggests an activated diffusion rather than viscous flow mechanism. For uncoated paper, the measured diffusion coefficients range from 9×10^{-9} to 4×10^{-10} cm.²/sec. For a typical activated diffusion process, the diffusion of water in cellulose acetate,⁸ the diffusion coefficient is 9×10^{-9} cm.²/sec. It therefore appears that the diffusion coefficients obtained in this investigation approach the range where activated diffusion is operative.

Comparison of Cellulose with Noncellulosic Materials

The rate of diffusion of ethylene-1,2-C¹⁴ glycol through a TiO₂-clay coating in a resinous (starch-latex) binder is two orders of magnitude slower than that through pure cellulose; the diffusion coefficient is only 7.8×10^{-11} cm.²/sec. With a substrate composition of this complexity, several types of permeation process could be taking place. The nature of the diffusion will depend on interaction between the solid and ethylene glycol, capillarity of the coating, and the barrier properties of the polymer.

The slow rates of diffusion observed in this system should be emphasized. It is felt that this technique has general applicability to various types of membranes and may be applied with advantage to systems with low diffusion rates, and/or where only small quantities of diffusant are available for investigation.

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Résumé

La diffusion de faibles quantités de liquides à travers des substrats polymériques poreux a été étudiée en utilisant des techniques aux radiotraceurs. Le procédé a été appliqué à la perméabilité de cinq types différents de papiers avec de l'éthylène glycol

1-2-C¹⁴. Les résultats indiquent que dans les conditions expérimentales utilisées l'analogie de diffusion est valable pour la pénétration du solvant dans les systèmes étudiés. La méthode devrait avoir une applicabilité générale aux études de vitesses de diffusion dans les membranes cellulosiques ou autres et à des études où uniquement des faibles quantités de substances diffusantes sont disponibles.

Zusammenfassung

Die Diffusion kleiner Flüssigkeitsmengen in porösen Polymersubstraten wurde mit einem Radiotracerverfahren untersucht. Das Verfahren wurde auf die Permeation von Äthylen-1,2-C¹⁴-Glykol durch fünf verschiedene Papiertypen angewendet. Die erhaltenen Ergebnisse zeigen, dass unter den Versuchsbedingungen die Analogie zur Diffusion für das Eindringen von Lösungsmittel in die untersuchten Systeme gültig ist. Die Methode sollte zur Untersuchung von Diffusionsgeschwindigkeiten in Zellulosemembranen und anderen Membranen allgemein anwendbar sein und besonders für Untersuchungen, bei welchen nur kleine Mengen des Diffusionsmittels vorhanden sind.

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