Permeability Studies with Crosslinked Cellophane

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Synopsis

Evidence for the crosslinking of cellulose by chemical treatment has been discussed by numerous authors.   In the present investigation an effort is made to determine whether such a structural change in cellulose may be inferred from a change in permeability.   The effect of a dialdehyde starch crosslinking treatment on the permeability of cellophane to potassium chloride ions from dilute solution is studied.   Diffusion coefficients are calculated and compared.   To account for sensitivity of diffusion results to the microstructure of the cellophane, it is assumed that under the experimental conditions a significant portion of the transport of ions across the membrane may take place by a process of activated diffusion directly through the polymer network.   It is suggested that the crosslinking treatment binds adjacent cellulose chains together creating a more rigid network structure which should resist penetration by diffusing ions.

INTRODUCTION

Although several varied crosslinking treatments for cellulose are described in the literature,[1-6] chiefly in connection with the addition of desirable physical characteristics to cellulose products, neither the presence of crosslinkages nor their correlation with these physical properties has been easy to demonstrate.   The study of physical properties imparted to cellulose by such treatments has been of continuous interest[7-9] since effective chemical treatment was first reported.[10]   The nature of the observed physical changes (e.g., reduction of swelling in solvent, increase of dimensional stability) has prompted many investigators to attribute them to crosslinking of the cellulose.[11]   This interpretation has gained additional support from chemical evidence of covalent crosslinkages in these systems such as that found by Wagner and Pacsu[12] in their detailed analysis of the exhaustive methylation products of formaldehyde treated cellulose.

Attempts to correlate changes in cellulose physical properties with crosslinking continue to be handicapped by the lack of a suitable theoretical approach.   Although corresponding relationships established in work with crosslinked rubbers and synthetic polymers have been shown[13] to be useful in predicting the course of physical change produced by cellulose crosslinking treatments, these relationships fail in any quantitative application to the cellulose data.

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Moreover, much of the accumulated cellulose physical data may be of questionable value as evidence for crosslinking, since physical changes attributable to crosslinking are frequently difficult to distinguish from those which are due to side effects of the treatment. For example, the reduced swelling of cellulose after a crosslinking treatment may also reflect changes in polymer morphology resulting from harsh conditions imposed by the treatment. The degradation of cellulose in the presence of water vapor at the elevated temperatures used in the crosslinking treatments has been reported[14] to lead to decreases in swelling through increased crystallinity.

In light of results obtained in the present investigation we wish to report some progress in the study of crosslinking in cellulose independent of the various possible side effects of the crosslinking reaction. We have chosen a physical chemical approach in which a study is made of the effect of a crosslinking treatment on the permeability of cellulose (cellophane) membranes to potassium chloride ions from dilute aqueous solution. The apparent rates at which the ions diffuse through treated cellophane and untreated cellophane are compared. In addition, various analytical techniques are employed to characterize the cellophane before and after treatment.

Cellophane membranes were given a crosslinking treatment with dialdehyde starch. (The acid-catalyzed treatment of cellulose with aldehydes has been extensively studied.[15]) Experimental problems encountered in the use of volatile low molecular weight aldehydes are avoided by use of the aldehyde polymer.

It was hoped that the binding of the cellulose network into a more rigid structure by permanent covalent crosslinkages could be demonstrated by a measurable decrease in permeability. The success of this approach would depend strongly on how sensitive diffusion results would be to the microstructure of the membrane.

Preliminary results had indicated that the rate of diffusion of potassium chloride ions through cellophane from dilute solution is several orders of magnitude less than that which would be expected from a self-diffusion through pores. McBain and Stuewer[16] had also observed this high salt retention.

It is an accepted characteristic of diffusion through pores that the diffusing species be required to traverse a tortuous path of length greater than the membrane thickness. The high salt retention observed in the present case may therefore be understandable, since diffusion of the solvated ions through any such tortuous system from a dilute solution may be a very slow and inefficient process. Furthermore, it is conceivable that when the overall rate of transport of diffusant across the membrane becomes low enough, some other normally less efficient transport mechanism may begin to compete with that of pore-type diffusion. Thus diffusion of the ions along the more direct route through the polymer network may come to play an increasingly important role in the permeation process,

(Ticknor[17] has assembled evidence to show that such an alternate diffusive type of transport, in addition to simple viscous flow, may contribute to permeation of cellophane by liquids under a pressure gradient.) This transport of the ions through the swollen polymer network by a process of activated diffusion[18] would, unlike a diffusion in water-filled pores, be dependent on the cooperative motion of polymer segments and ought to be sensitive to changes in molecular structure which affect their mobility.

In the ensuing diffusion studies the calculation of diffusion coefficients is based on a simple derivation which is now given. Barrer[19a] has provided a treatment of Fick's first law of diffusion which can be used to determine the diffusion coefficient, D, from measurements as a function of time, t, of the total amounts of solute, Q, which has diffused across a unit cross-sectional area of the membrane.

$$Q = - \int_0^t D(dC/dx)dt \qquad (1)$$

If the total amount of solute diffused is small, it becomes reasonable to assume that the gradient of solute concentration is essentially unaltered during the course of the experiment. If the gradient of solute concentration across the membrane is assumed to be linear, eq. (1) takes the following simplified form:

$$Q = -D(C_1 - C_2)(\Delta t)/h \qquad (2)$$

where C_1 and C_2 are the concentration of diffusant (solute) at the ingoing and the outgoing faces of the membrane, respectively, and h is the thickness of the membrane. In a preliminary test of eq. (2), diffusion experiments were conducted at two relatively widely divergent C_1 concentrations, $0.002M$ and $0.01M$. The diffusion coefficients calculated from these data are in reasonably good agreement with each other.

EXPERIMENTAL

Materials

Additive-free cellophane (1 mil in thickness) was obtained from E. I. du Pont de Nemours & Company.

Dialdehyde starch, supplied under the trade-name Sumstar, is manufactured by Miles Chemical Company, Division of Miles Laboratories Incorporated.

Radioactive $Co^{60}Cl_2$ was procured through Union Carbide Corporation, Oak Ridge, Tennessee.

Pyridine hydrochloride was obtained as the reagent grade from Eastman Organic Chemicals Company.

Sodium dodecyl sulfate was obtained from Cole-Matheson-Bell Company and purified before use by Soxhlet extraction with ether and absolute ethanol.

Crosslinking Treatment

An aqueous 10% solution of dialdehyde starch, containing 0.1% of pyridine hydrochloride as catalyst and a trace of sodium dodecyl sulfate wetting agent, was painted on the dry cellophane surface. While still wet, the membrane was suspended over warm water in a Pyrex vessel. The vessel was then sealed and placed in an oven. The membrane, suspended inside the vessel, was allowed to react in the hot water vapor atmosphere at 130°C. for 15 min. The treated membrane was then leached free of remaining reactant and any water-soluble impurities by successive soakings in distilled water.

Diffusion Experiments

The Pyrex diffusion cell used was of the two-chambered, single-membrane type. The mounted membrane was held in place between the abutting flanges of the cell halves by means of spring clamps. Dow Corning high vacuum silicone grease functioned as the sealant between the membrane and flanges.

The diffusion was begun by adding simultaneously an aqueous $0.002M$ potassium chloride solution to one chamber, and distilled water to the other chamber. A conductivity cell suspended in the distilled water and connected to a Wheatstone bridge circuit was used to measure the resistivity of the water as ions diffused through the membrane from the solution in the other chamber. Change of resistivity was equated to increase in potassium chloride concentration by reference to the conductivity cell calibration curve. Stirring on this dilute side of the diffusion cell was accomplished by means of a magnetic stirring apparatus. Diffusion time was measured with a stopwatch, and the collection of data was begun at the 7.5×10^5 ohm resistivity level in the distilled water side of the diffusion cell.

Water Permeability Measurements

The same type of diffusion cell was used in water permeability measurements. The membrane to be studied (after a previous equilibration with distilled water) was mounted between the greased flanges of the cell halves and held in place by means of spring clamps. The two cell chambers thus formed were then filled with distilled water. Pressure (0.05–0.1 atm.) was applied to one of the chambers by means of a water column which was adjustable in height. Increases in the volume of water in the chamber on the other side of the membrane were detected by means of a uniform bore glass capillary attached to the top of the chamber. The capillary was fixed in a horizontal orientation so that the volume of water entering it during the experiment could not generate a hydrostatic pressure difference between the two cell chambers. The rate of flow of water through the membrane under the applied pressure gradient was measured by observing the advance of the meniscus along the capillary

as a function of time. Each centimeter of its travel along the capillary corresponded to 2×10^{-2} cm.^{3} of water which has come through the membrane.

In the determination of effective pore size from water permeability data several assumptions may be made which grossly simplify the calculation. If the "pores" are assumed to be straight and cylindrical and to be equal in length to the membrane thickness, Poiseuille's law can be applied. The permeability of the membrane may then be expressed as:

$$A = N\pi r^4/8L\eta \tag{3}$$

where L is the thickness of the membrane, η is the viscosity of water, and r is the effective pore radius. It is possible to express N, the effective number of pore openings per unit surface area of the membrane, in a more useful form. From the work of Madras, McIntosh, and Mason[20] the fractional void volume, ϵ, of cellophane is given as 0.59. If the fractional void volume and the fractional void surface may be considered as equivalent values, N can be expressed as $\epsilon/\pi r^2$ and eq. (3) rewritten in the form:

$$r = (8AL\eta/0.59)^{1/2} \tag{4}$$

from which the effective pore radius can be calculated readily.

Absorption Studies

A radioactive solution of cobalt chloride (Co[60]) absorbate was prepared by adding a trace quantity of the labeled compound to distilled water. The cobalt chloride concentration was then brought up to $0.002M$ by adding nonradioactive cobalt chloride. Disks, 5 cm.^{2} in area, were punched from the various membranes and immersed in the radioactive solution for periods ranging from 4 sec. dips to overnight equilibrations. On removal from solution each disk was given a quick dip in distilled water in order to remove excess clinging solution and blotted dry with filter paper. Rinse water was changed for each sample. The dried disks were mounted on cardboard and autoradiographed.

Swelling Studies

The swelling of membrane samples was estimated from the percentage weight gain of samples after an overnight equilibration in distilled water. On removal from the water individual samples were quickly blotted with filter paper, immediately placed in a glass stoppered weighing bottle, and weighed on an analytical balance.

RESULTS AND DISCUSSION

In the preliminary examination of membranes to be used in the diffusion studies the surfaces of crosslink-treated and untreated cellophane were compared by means of electron microscope photographs such as those shown in Figures 1 and 2. The relative smoothness of the treated mem-
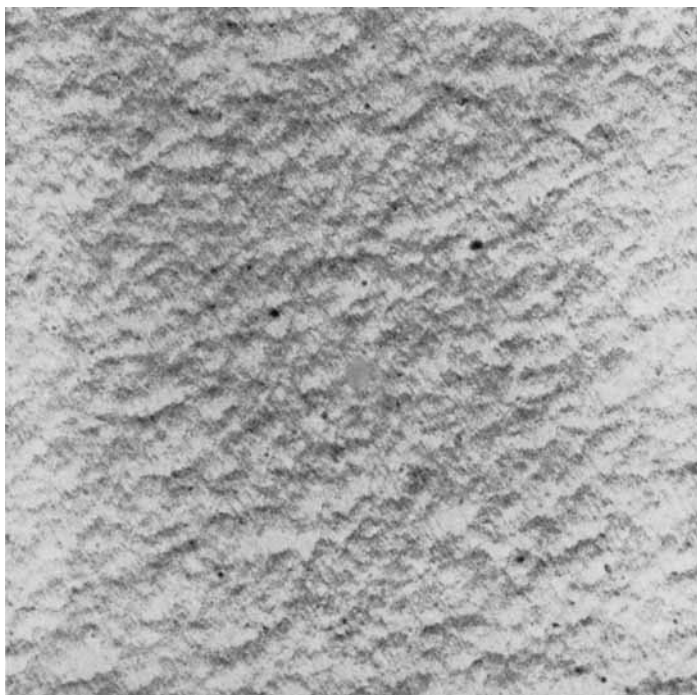
Fig. 1. Electron microscope photograph of untreated cellophane from a direct (single-stage) carbon replica, shadowed with palladium at an angle of $\tan^{-1} 0.2$. Direct magnification 17,000X. Enlarged to 34,000X.

brane surface (Fig. 2) suggests that the crosslinking treatment with dialdehyde starch may deposit a coating. Careful inspection of the photograph reveals mottled (mounded) areas, the pattern of which resembles surface irregularities in the natural cellophane shown in Figure 1. Such a coating would be extremely thin.

Barrer[19b] has mentioned that even very thin coatings (e.g., the wax coating which is applied to cellophane in commercial moisture-proofing treatments) may produce a marked change in membrane permeability. It is commonly supposed that the effectiveness of thin coatings as barriers to diffusion through cellophane depends largely on the physical blocking of "pores" at the membrane surface.

The effect of the crosslinking treatment on the porosity of cellophane was therefore investigated. The effective pore sizes of the treated and the untreated samples were calculated from the membrane permeability to liquid water. The apparatus used for the determination of water permeability, similar to that used by White,[21] is described in the previous section. A comparison of pore radius values obtained for treated cellophane ($r = 1.55 \times 10^{-7}$ cm.) and for untreated cellophane ($r = 1.60 \times 10^{-7}$ cm.) suggests that the treatment introduces no physical barrier to permeation. Both values are in excellent agreement with the effective
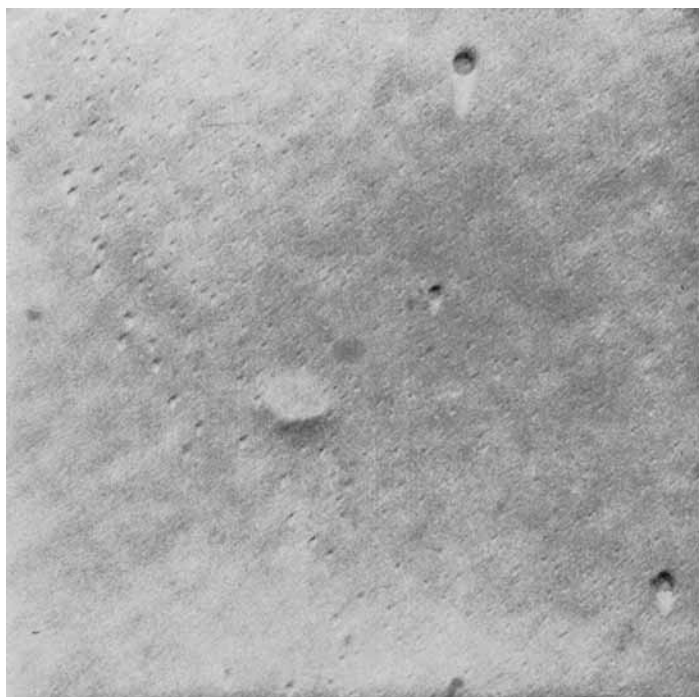
Fig. 2. Electron microscope photograph of crosslink-treated cellophane (for sample preparation see Fig. 1). Total magnification 34,000×.

pore radius of cellophane ($r = 1.5 \times 10^{-7}$ cm.) as reported by Madras et al.[20]

Samples of treated and untreated membranes were also tested for swelling. It was noted that cellophane treated with dialdehyde starch tended to curl when first dipped in the swelling medium (water), and swelled at equilibrium (see Table I) only one-third as much as did the untreated cellophane. Although dialdehyde starch is a polymer and had been expected to "treat" only the cellophane surface, it was concluded from the observed reduction in swelling that lower molecular weight fractions of it may diffuse more deeply into the membrane before reacting.

TABLE I
Swelling of Treated and Untreated Cellophane Samples in Distilled Water

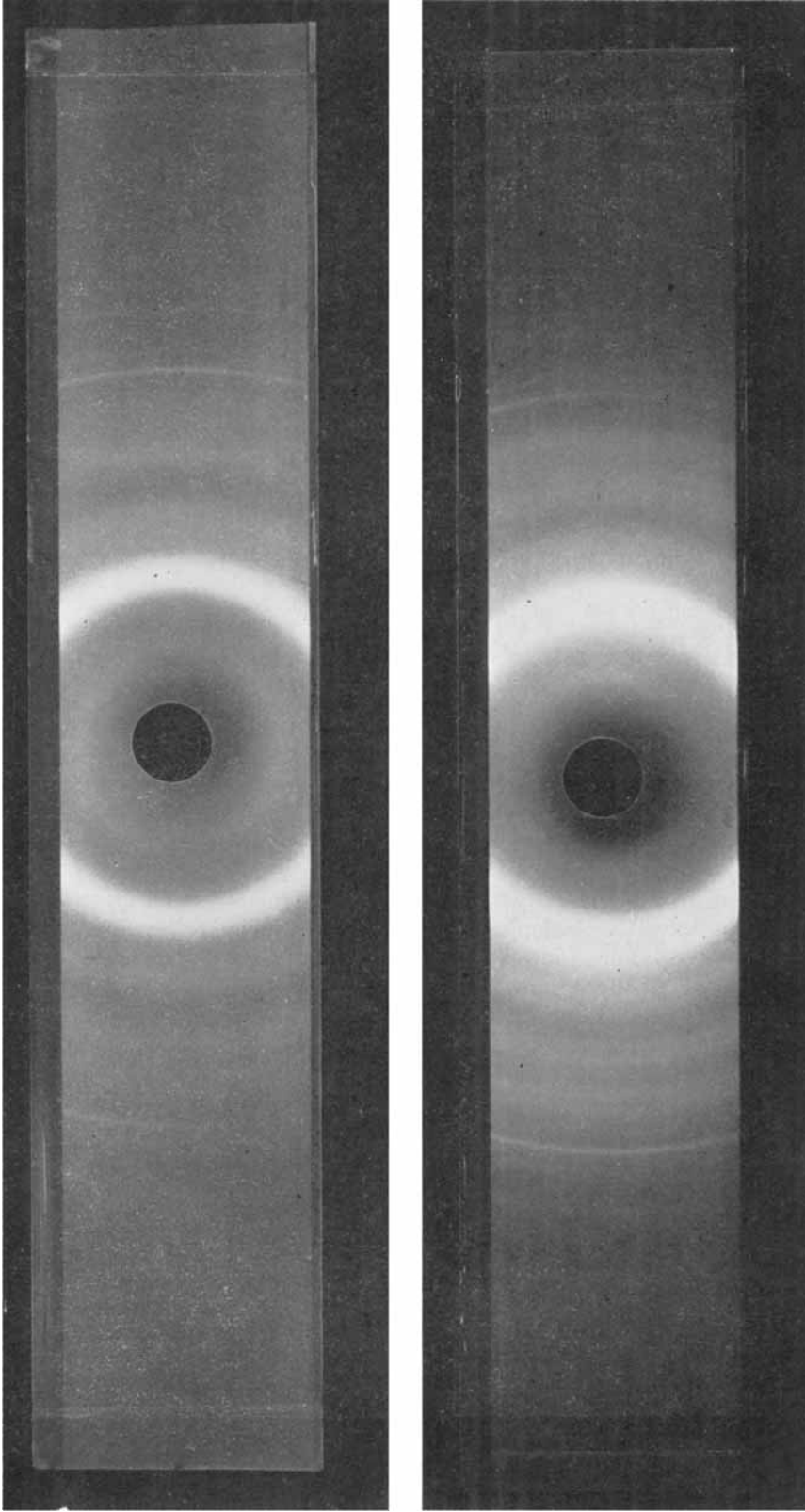| Sample	Initial dry weight, g.	Final swollen weight, g.	Increase in weight, %
Untreated	0.0886	0.1739	96.3
Watered, and baked	0.0820	0.1403	71.1
Crosslink-treated	0.0942	0.1224	29.9

Fig. 3. X-ray diffraction patterns of (top) untreated and (bottom) crosslinked-treated cellophane determined from rolled strips of sample with a Debye-Scherrer powder camera using nickel-filtered Cu K_α radiation and a specimen-to-film distance of 6 cm.
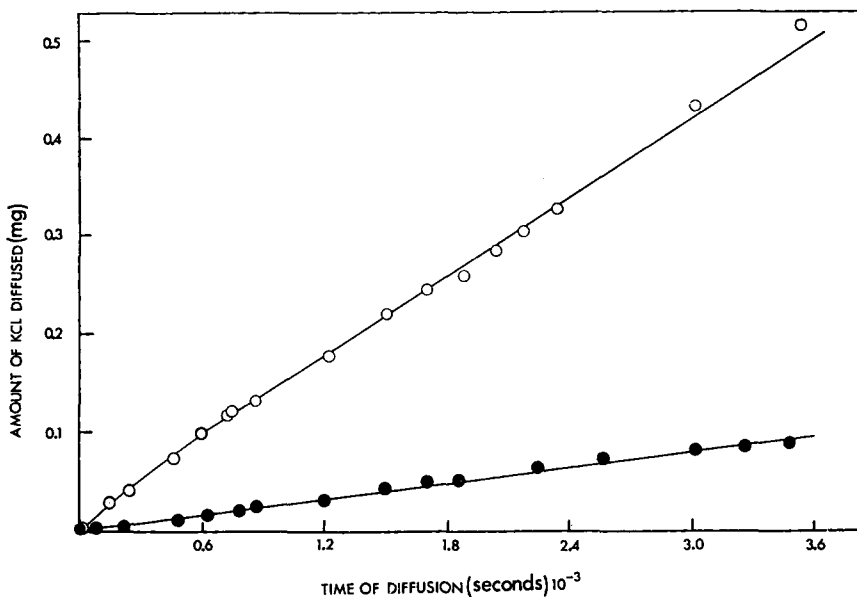
Fig. 4. Effect of crosslink treatment on diffusion of potassium chloride through cellophane: (O) untreated cellophane; (●) crosslink-treated cellophane.

Evidence in favor of the crosslinking hypothesis is found in the x-ray diffraction patterns of treated and nontreated cellophane shown in Figure 3. The marked broadening and intensification of the diffuse band in the pattern obtained from treated cellophane indicates that the crosslinking treatment results in a decrease in cellophane crystallinity. Therefore it cannot be argued that the reduced swelling of the treated cellophane is caused by the increase in crystallinity usually associated with the wetting and redrying of cellulosic materials. Moreover, the detected decrease in crystallinity would be an understandable consequence of the formation of interchain crosslinks in the swollen polymer network during treatment.

Diffusion studies subsequently revealed that the crosslinking treatment causes a fivefold reduction in cellophane permeability to potassium chloride ions. Typical data comparing a treated and an untreated membrane are plotted in Figure 4. Diffusion data were readily reproduced on different occasions and with separately prepared membranes. One of the treated membranes, stored in water for six months after its original use, accurately reproduced the original diffusion curve.

The less marked decrease in permeability (see Fig. 5) caused by wetting cellophane with distilled water and baking in a water vapor atmosphere as in the crosslinking treatment may arise through the possibility of molecular rearrangement on wetting followed by gradual formation of a more ordered and compact molecular network during baking.[22] These membranes also swelled less than the untreated cellophane (see "watered and baked," Table I). The x-ray diffraction method (results not indicated) was unable
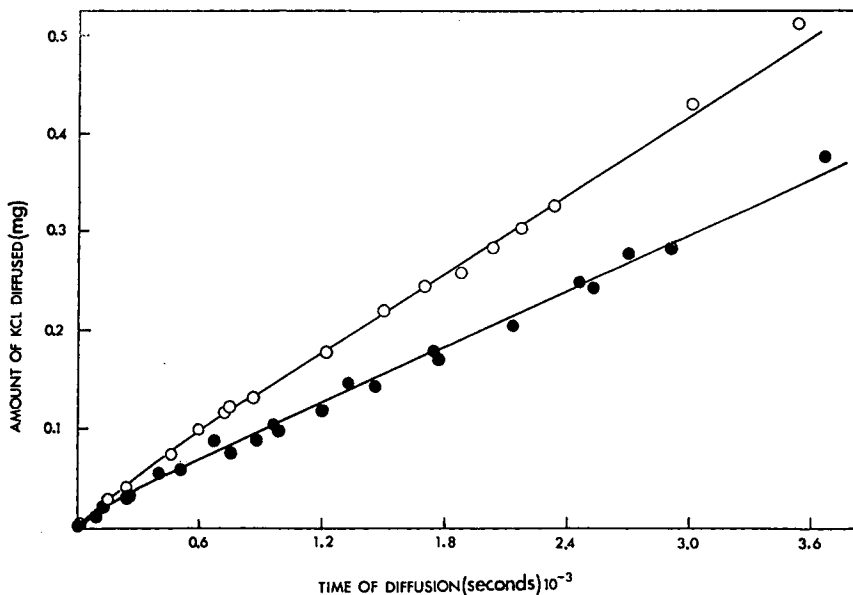
Fig. 5. Effect of wetting and baking on diffusion of potassium chloride through cellophane: (O) untreated cellophane; (●) watered and baked cellophane.

to distinguish a difference in crystallinity between these and the untreated cellophane membranes.

The diffusion data are summarized in Table II, which lists the diffusion coefficients calculated according to eq. (2).

McBain and Stuewer[16] attributed the general low permeability of cellophane to ions from dilute solution to the presence of theoretical fixed charges along the walls of pores in the membrane. They explained that these fixed charges act to repel dilute electrolyte, simulating a reduced size of pore in diffusion measurements.

Before attempting to explain the data from the present work, it is therefore necessary to determine whether similar effects may be operative in the observed changes in cellophane permeability following a crosslinking treatment. If this decreased permeability to potassium chloride ions represents an increase in the number of charged groups per unit volume of membrane

TABLE II
Coefficients of Diffusion of Potassium Chloride through Untreated and Crosslink-Treated Cellophane

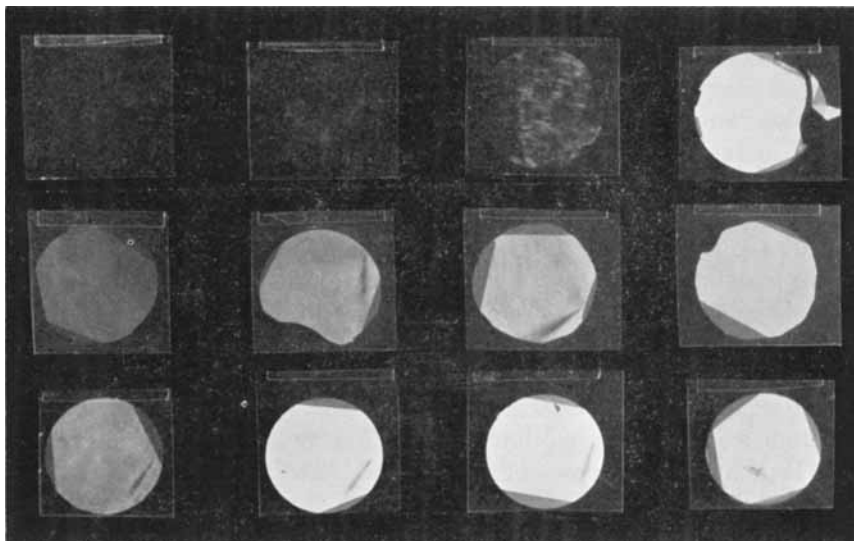| Sample	KCl diffused, mg./hr.	Average concentration gradient, moles/l. $\times 10^{-3}$	Diffusion coefficient, cm.^{2}/sec. $\times 10^{-7}$
Untreated	0.511	1.983	2.81
Crosslink-treated	0.094	1.997	0.43

Fig. 6. Autoradiographs of cellophane disks from sorption experiments with radio-active cobalt chloride absorbate. Direct prints from the exposed negatives represent two week contact of samples with Ansco Super-Hypan photographic film. Sorption times (from left to right) are 4, 30, and 60 sec. dips, and overnight equilibrations; top row shows crosslink-treated cellophane, middle row is watered and baked cellophane; bottom row is untreated cellophane.

(which may be interpreted as a decrease in the solubility of potassium chloride ions in the membrane), crosslink-treated cellophane should absorb less electrolyte from a dilute solution than does either the nontreated or the "watered and baked" membranes.

Radiological techniques were therefore developed in order to compare the absorption of an electrolyte (cobalt chloride) from a dilute aqueous solution by each type of membrane. Cobalt chloride (Co^{60}) was used in preparing a radioactive solution of about the same molar concentration as that of the potassium chloride in the diffusion studies. The experiment is described in the previous section. Autoradiographs of membranes which had been dipped in the solution for various time periods (shown in Fig. 6) establish that while the initial uptake of electrolyte follows the same order as the relative rates of permeation of cellophane by electrolyte in the diffusion experiments, the quantity absorbed always approaches the same equilibrium value. Therefore the solubility of ions in cellophane does not seem to be appreciably altered by the crosslinking treatment.

CONCLUSION

As a point of departure for the present investigation it was contended that the rate of diffusion of ions through cellophane from dilute solution may be sensitive to changes in the molecular structure of the membrane which affect segmental mobility in the polymer network. Specifically, it

was suggested that the crosslinking of cellophane with dialdehyde starch may be detectable as a reduction in membrane permeability to potassium chloride ions in dilute aqueous solution. To account for sensitivity of diffusion rates to the microstructure of the membrane an alternate, activated, diffusion mechanism capable of successful competition with the pore-type of diffusion at low rates of permeation was proposed.

The diffusion coefficients determined in the investigation which followed range as low as 4×10^{-8} cm.²/sec. A value for the diffusion coefficient in a typical activated diffusion process (the diffusion of helium through dry cellophane) is 0.12×10^{-8} cm.²/sec. Therefore the measured rates of diffusion of potassium chloride ions through cellophane approach a range where activated mechanisms may be competitive. Diffusion coefficient values determined in this study may be somewhat large due to the contribution from self diffusion through voids in cellophane. This void volume may be reduced in the case of "watered and baked" cellophane causing the observed decrease in diffusion rate. The use of water-swollen rather than dry cellophane may also be expected to exert a sizeable influence on the activated diffusion rate. Barrer[19c] has suggested that in activated diffusions swollen membranes may be more permeable than dry ones, because of a loosening of the polymer network.

Since the crosslinking treatment with dialdehyde starch appears to have no demonstrable affect on the porosity of cellophane, and actually appears to reduce the crystallinity, it follows that the fivefold reduction in permeability brought about may reflect chiefly the affect of added acetal crosslinkages on segmental mobility in the polymer network. Reid and Kuppers[23] have noted the reduced ion permeability of cellophane crosslinked with cupric ion.

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Résumé

Divers auteurs ont discuté le problème du pontage de la cellulose par un traitement chimique. Dans le présent travail on a principalement cherché à déterminer si une telle variation dans la structure de la cellulose peut être constatée à partir d'une variation de perméabilité. On a étudié les conséquences du traitement par un agent de pontage dial-déhydique, sur la perméabilité de la cellophane, aux ions provenant d'une solution diluée de chlorure de potassium. Les coefficients de diffusion ont été calculés et comparés. Pour expliquer la sensibilité des résultats de mesures de diffusion vis-à-vis de la micro-structure de la cellophase, on suppose que, dans les conditions expérimentales, la majeure partie du transport des ions à travers la membrane peut s'effectuer par un processus de diffusion activée directement à traverse le réseau du polymère. On èmet l'hypothèse que le traitement responsable du pontage réunit des chaînes cellulosiques adjacentes en créant une structure réticulaire plus rigide qui résisterait à la pénétration des ions diffusants.

Zusammenfassung

Die durch chemische Behandlung hervorgerufene Vernetzung von Cellulose wurde schon von zahlreichen Autoren diskutiert. In der vorliegenden Arbeit wurde zu klären versucht, ob auf eine derartige strukturelle Veränderung von Cellulose aus einer Perme-abilitätsänderung geschlossen werden kann. Der Einfluss einer vernetzenden Dialdehyd-Stärkebehandlung auf die Permeabilität von Cellophan gegenüber Kaliumchloridionen aus verdünnter Lösung wurde untersucht. Die Diffusionskoeffizienten wurden berechnet und verglichen. Zur Erklärung der Empfindlichkeit der Diffusionsdaten gegenüber der Mikrostruktur des Cellophans wird angenommen, dass unter den gegebenen experi-mentellen Bedingungen ein wesentlicher Teil des Transportes der Ionen durch die Mem-bran in einer aktivierten Diffusion direkt durch das Polymernetzwerk besteht. Durch die Vernetzungsbehandlung werden offenbar benachbarte Celluloseketten zu einer starreren Netzwerkstruktur verunden, die dem Eindringen diffundierender Ionen Wider-stand leisten sollte.