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WATER VAPOR PERMEABILITY IN A POLYESTER BASED POLYURETHANE

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INTRODUCTION

The sorption, diffusion and interactions of water vapor with polymers is of widespread importance to Army material requirements. Environmental water can have a profound effect on the performance of polymers through its influence on mechanical behavior alone or its contribution to hydrolytically induced polymer chain scission. Moreover, the mechanism of water transmission is important in a variety of protective applications such as packaging films, corrosion resistance coatings and the like. In the present work, the main emphasis has been on the study of the mechanism of water vapor transport in polymers with high moisture vapor transmission rates (MVTR's) that might serve as physiologically comfortable barrier films. Such polymers would be useful as fabric coatings for rainwear or for Chemical-Biological (CB) agent protection if the coating were resistant to agent vapors. The importance of such a development hardly needs to be emphasized since it would open the door to a significant new approach to achieving chemical protection as part of the combat clothing issue.

To date there has been little progress in the development of polymers having MVTR's which are sufficiently high to serve as physiologically acceptable barrier films. However, certain commercial polyurethane elastomers offer MVTR's which are on the threshold of the range needed for physiological benefit. The benefits conferred even by the limited MVTR of these polyurethanes have been demonstrated in climatic chamber tests at Natick Laboratories. Volunteer subjects wearing air impermeable coveralls coated with neoprene rapidly succumbed to heat exhaustion whereas test subjects in polyurethane coated coveralls survived 2 hours at rest followed by a 50 minute walk under tropical conditions. The latter subjects were uncomfortable but remained active.

The work presented in this paper was undertaken to gain an improved understanding of the factors controlling water vapor transmission in polyurethanes. Polyurethanes were chosen as candidate materials because of their favorable MVTR's. In addition, since polyurethanes are block copolymers, they offer numerous possible variations in the nature, length and proportions of the alternating long flexible and short hard segments that constitute the polymer chain. The study was expected to provide a basis for determining whether and by what means polyurethanes with the required high MVTR's could be designed. In addition, the study was expected to shed light on the general mechanism of water vapor sorption and diffusion which is important to other polymer applications.

THEORY

Consider a polymer film of uniform thickness l with a difference in the concentration of penetrant molecules $\Delta c = c_2 - c_1$ across the film. According to Fick's first law(1,2) the flux of penetrant molecules J in grams or cm.^{3} per unit area and per unit time is proportional to the concentration gradient dc/dl

$$J = - D \frac{dc}{dl}$$

The constant of proportionality D is known as the diffusion constant. If the film is exposed to vapor at a pressure p_2 on one side and $p_1 < p_2$ on the other side and if the solubility of the vapor in the polymer is governed by Henry's law

$$c = kp$$

then the flux can be expressed in terms of the pressure gradient

$$J = -Dk \frac{dp}{dl}$$

Thus, the rate of transmission of penetrant per unit pressure gradient is governed by the product of a thermodynamic factor and a kinetic factor. The thermodynamic factor is the Henry's law solubility constant k which depends solely on the polymer-penetrant interactions. The kinetic factor is the diffusion constant D which is governed by the rate of the polymer segmental motion and the size of the penetrant molecules. The product Dk is termed the permeability coefficient P and in an ideal system would be independent of the experimental conditions.

In attempting to understand the relation between the polymer structure and moisture vapor transmission rates it will be necessary to resolve P into its component factors and relate these separately to the polymer structure.

EXPERIMENTAL METHODS

Steady state transmission rates were determined using cup cells containing water and sealed with the polymer film. The cells were placed in an air stream maintained at 70°F and 50°% R H and the loss in weight due to evaporation of water across the film was measured at timed intervals. The results were converted into values of the flux or the permeability coefficient as required from a knowledge of the film area, film thickness and relative humidity difference. The water solubility was determined from the weight gain of the sample immersed in water. In combination with P this permits a calculation of the effective D as the ratio P/k.

While the parameters obtained from these measurements are useful in comparing different polymers, this method does not provide data which are needed to understand the complex behavior exhibited by water vapor. In particular, it is not possible to vary the concentration of water in the polymer as required to determine the sorption isotherm or the dependence of the diffusion constant on concentration. For this purpose a vacuum-sorption system was used in which the sample could be exposed to a selected vapor pressure of water and the weight gain measured with a Cahn electro-balance or quartz spring. Diffusion constants were calculated by standard methods(1,2,3) from the rate of water uptake and the solubility was obtained from the final constant weight of the sample at the particular vapor pressure.

SAMPLES

An initial survey was conducted on several commercial or exploratory polyurethanes of incompletely specified composition but the main body of the work was concerned with a series of structurally varied polyurethanes. All were composed of a polyester or polyether (molecular weight 2,000), (1,4)-butanediol and MDI in the mole ratio 1:3.2:2. They differed only in the nature of the flexible segment which included polybutylene adipate and three polyethers representing an increasing frequency of ether linkages in the order polytetramethylene oxide PTMO, polypropylene oxide PPO, and polyethylene oxide PEO.

MOISTURE VAPOR TRANSMISSION RATES OF TYPICAL POLYURETHANES

The moisture vapor transmission rates of three commercial and one exploratory polymer (LD - 550) appear in Table I expressed as the flux for a one mil thick film. Since all of these samples have a water solubility of about 2%, the nearly eight-fold variation in permeability which occurs in this group of polymers must arise solely from differences in the apparent diffusion constant for water.

The diffusion of penetrant molecules in a rubbery polymer matrix can be represented as occurring by a process of jumping into holes created by the cooperative motion of the polymer segments. In effect, the penetrant diffusion constant is determined by the rate of polymer segmental motion. It is well established that the rate of segmental motion for all polymers is described by a nearly universal function which depends only on the difference between the experimental temperature and the glass transition temperature $\Delta T = T - T_g$(5). (The glass transition temperature is the point at which the the sample transforms from a rubbery to a glassy solid due to the freezing out of segmental motion.) In turn, this implies that in comparing polymers at a fixed temperature, the diffusion constant, like the rate of segmental motion, will be larger if the glass transition temperature is lower. The comparision in the last column of Table I shows that this prediction is true, suggesting that for polymers with equal water solubilities, the polymer with the lower Tg will have the higher permeability. However useful such a rule proves to be on a qualitative basis, it fails quantitatively since theory predicts a one-hundred fold rather than an eight-fold range in MVTR for the differences in Tg corresponding to these polymers.

RESULTS ON STRUCTURALLY VARIED POLYURETHANES

The relevant parameters characterizing the steady state transmission of water vapor in the series of structurally varied polyurethanes are listed in Table II. The water solubility changes very little in the first three samples but undergoes a spectacular increase in the PEO type of polyurethane.

Taking the results for the PBA sample as the basis of comparison, consider first the behavior of the PTMO sample. Since PTMO-PU has a much lower Tg, it would have been expected that the permeability would be much higher than for the PBA sample, in keeping with the comparative behavior of the commercial polyurethanes. In fact, the permeability of the PBA and PTMO samples are nearly the same, whereas theory predicts a 35 times higher value for the latter sample. There is another inconsistancy in this set of results. In the PEO sample the water concentration is 80 times higher than in the PBA sample and yet the permeability has increased only 7 times. Since Tg is the same for these two polymers, it would have been expected that the increase in permeability would equal the 80 times increase in water concentration. These two comparisons indicate that the water permeability cannot be predicted simply from a knowledge of the concentration of water or the glass transition temperature. The behavior is complicated by additional considerations which can be understood only by examining the component factors of the permeability coefficient in more detail.

Before proceeding further it would be useful to compare the MVTR of these films with values of practical interest. An MVTR of about 40g./100 in.^{2}/24 hours is required for perceptible heat relief while the MVTR for standard cotton poplin (5.3oz./yd.^{2}) is about 650g./100 in.^{2}/24 hours. For all the polymers the values of J1, which represent the MVTR for a one mil film, exceed the minimum required value. The value of the unnormalized flux J for the PEO sample exceeds even that for cotton poplin. The usual normalization to one mil thickness does not hold for this sample and is omitted from the Table II.

POLY(BUTYLENE ADIPATE) POLYURETHANE

The sorption isotherm obtained by the vacuum sorption method is shown in Figure 1. The water concentration (g. water/cm.^{3} polymer) against the partial pressure or activity of water (p/po) is initially linear, approximating Henry's law behavior. However, above an activity of 0.6 the isotherm turns concave upward in a manner typical of polar sorbents in polar substrates. Unexpectedly it was found that the isotherms determined at different temperatures were superimposable. This signifies that the heat of mixing for water with the polyurethane is zero(1). Accordingly, it appears that the environment of water molecules dissolved in the polymer is energetically equivalent to that of liquid water. The dependence of the diffusion constant on the water concentration in the polymer is shown in Figure 2. The diffusion constant decreases with increasing water concentration in marked contrast to the usual strong increase in the diffusion constant that occurs with the swelling of polymers by organic vapors(1).

The concave upward behavior of the sorption isotherm, the zero heat of mixing, and the decrease in the diffusion constant of water can all be attributed to the self association of the water molecules dissolved in the polymer matrix. The reconstitution of intermolecular hydrogen bonding among water molecules in clusters is responsible for the zero heat of mixing; the diminished activity of the increasingly clustered water, as compared to randomly distributed water molecules, increases the concentration of dissolved water and produces the concave upward isotherm(5): and the immobilization of water in clusters reduces the effective diffusion constant(6). Thus water clustering dominates the overall process of water vapor transmission in this polymer.

POLY (TETRAMETHYLENE OXIDE) POLYURETHANE

The question to be answered is whether clustering also occurs in this polyurethane and, if so, whether it accounts for the much lower than expected MVTR. Both the sorption isotherm and the curves representing the concentration dependence of the diffusion constant for this polymer so closely resemble those for the PBA-PU that it is unnecessary to reproduce them. This not only shows that water clustering dominates the MVTR of this polymer but also indicates that the extent of clustering is no greater than in PBA-PU. Another mechanism is required to explain the abnormally low apparent diffusion constant.

There is evidence that the low diffusion constant arises from the presence of organized amorphous structure in the PTMO-PU which results from association of the urethane regions of the polymer chains(7,8). Low angle x-ray scattering patterns provide direct evidence that such domain structure is present in the PTMO-PU but not in the PBA-PU(9) and this conclusion is supported by several lines of more indirect evidence(8). If these domains are impermeable to water, the diffusing molecule would be required to travel around the impediment, thus lengthening the diffusion path and decreasing the effective diffusion constant(11).

POLY (ETHYLENE OXIDE) POLYURETHANE

The sorption isotherm for this polymer (Figure 3) differs significantly from the behavior of the other two polymers and is marked by an almost exponential increase in concentration above an activity of 0.5. This strong concave upward curvature indicates that a larger fraction of the water exists in the form of clusters than occurs in the other two polymers. The radical increase in the extent of clustering is also reflected in the precipitous drop in the diffusion constant with increasing water concentration (Figure 4). Thus, it can be concluded that the relatively limited increase in MVTR accompanying the large difference in water concentration, as compared to PBA-PU, is due to the immobilization of a much larger fraction of the water in clusters. However, it should be pointed out that in this instance the values of the diffusion constants obtained from the time dependence of the sorption are influenced by other effects(11,12) which tend to overemphasize the decrease in D with increasing concentration.

CONCLUSIONS

These studies provide considerable insight on the mechanism of water vapor transport in polyurethanes and open the way to the rational design of polymers with high moisture vapor transmission rates (MVTR's). Certainly the major conclusion revealed by this work is that the clustering of water dominates all aspects of the water transport process. In particular, clustering is responsible for the decrease in the effective diffusion constant which tends to offset the gain in permeability due to the increased water uptake. Behavior of this sort is undoubtedly not peculiar to the polyurethanes but probably occurs to a significant degree in other polymers as well. The previously unsuspected presence of domain structure, which occurs to varying degrees depending on the composition of the particular polyurethane, also acts to reduce the diffusion constant and the MVTR. These two factors, clustering and structure, complicate any simple correlation between MVTR's and such characteristic polymer parameters as the water solubility and the glass transition temperature.

Despite these effects it is evident that major changes in the MVTR can be achieved by suitable alteration of the polyurethane structure, even within the narrowly prescribed limits of the present study. For the most hydrophilic polymer, poly (ethylene oxide) polyurethane, the MVTR is competitive with the values for textile fabrics. However, in any practical application it would be necessary to limit the extent of swelling of the polymer by water. Fortunately, due to the counterbalancing effects of clustering on the diffusion constant and water uptake, it should be possible to design polymers with lower degrees of swelling at still acceptable moisture vapor transmission rates. There are several alternative ways of modifying PEO-PU. Films of suitable composition could be made from physical mixtures of the PEO- and PTMO- polyurethanes or mixing could be accomplished on a molecular basis using block or random copolymers incorporating the ethylene oxide repeating unit. In addition, high permeabilities might be achieved with polymers of another structure. In particular, ionic groups are known to destructure water and could minimize the intrusion of clustering. Although not included in this presentation, results have been obtained on polyion graft copolymers that do, in fact, show higher water vapor permeabilities at substantially lower swelling ratios.

TABLE I

MOISTURE VAPOR TRANSMISSION RATES FOR SEVERAL COMMERCIAL POLYURETHANES

Polyethers	J1 $\frac{\text{g-mil}}{100\text{in}^2\text{-24hrs.}}$ *	Tg°c
Du Pont LD-550	190	-60
Estane 574-140	84	-51
Polyesters		
Mobay PBA	68	-45
Estane 574-100	26	-18

Conditions for steady state transmission measurements: cup cells; inside, water in contact; outside, 40% RH, T= 90°F.

*The saturation water concentration was about 2% for all samples.

TABLE II

WATER SORPTION AND PERMEABILITY IN STRUCTURALLY VARIED POLYURETHANES

Sample	Thickness (mil)	Water Conc. g/100g	J(a)	J1(b)	Tg °c
PBA	11.2	1.6	6.9	78	-45
PTMO	12.5	1.8	4.3	64	-85
PPO	13.0	2.8	6.0	78	-50
PEO	14.0	126.0	780.0	--	-49

Conditions for steady state transmission measurements: cup cells; inside, water in contact; outside, 50% RH; T=70°F.

(a) g./100 in.^{2}/24hrs.

(b) g.-mil/100in.^{2}/24hrs.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the work of Elizabeth Snell and Robert Prosser.

REFERENCES

1. Rogers, C. E. in Engineering Design for Plastics, E. Baer (Ed), Reinhold Publ. Corp, New York, (1964), Chap. 9.
2. van Amerongen, G., J. Rubber Chem. Tech., 37, 1067 (1964).
3. Crank, J., The Mathematics of Diffusion, Oxford, London (1956), Chap. 1.
4. Ferry, J. D., Viscoelastic Properties of Polymers, John Wiley, New York (1961), pp 215 and ff.
5. Zimm, B. H., and J. L. Lundberg, J. Phys. Chem., 60, 425 (1956).
6. Barrie, J. A., and B. Platt, Polymer 4, 303 (1963).
7. Cooper, S. L., and A. V. Tobolsky, J. Appl. Polymer Sci., 10, 1837 (1966).
8. Clough, S. B., and N. S. Schneider, Polymer, in press.
9. Clough, S. B., A. King and N. S. Schneider, in preparation.
10. Michaels, A. S., and H. J. Bixler, J. Polymer Sci., 50, 393 (1961).
11. Rogers, C.E., Op. Cit. Chapter 8.
12. Fujita, H., Fortschr, Hochpolym.Forsch, 3, 1 (1961).

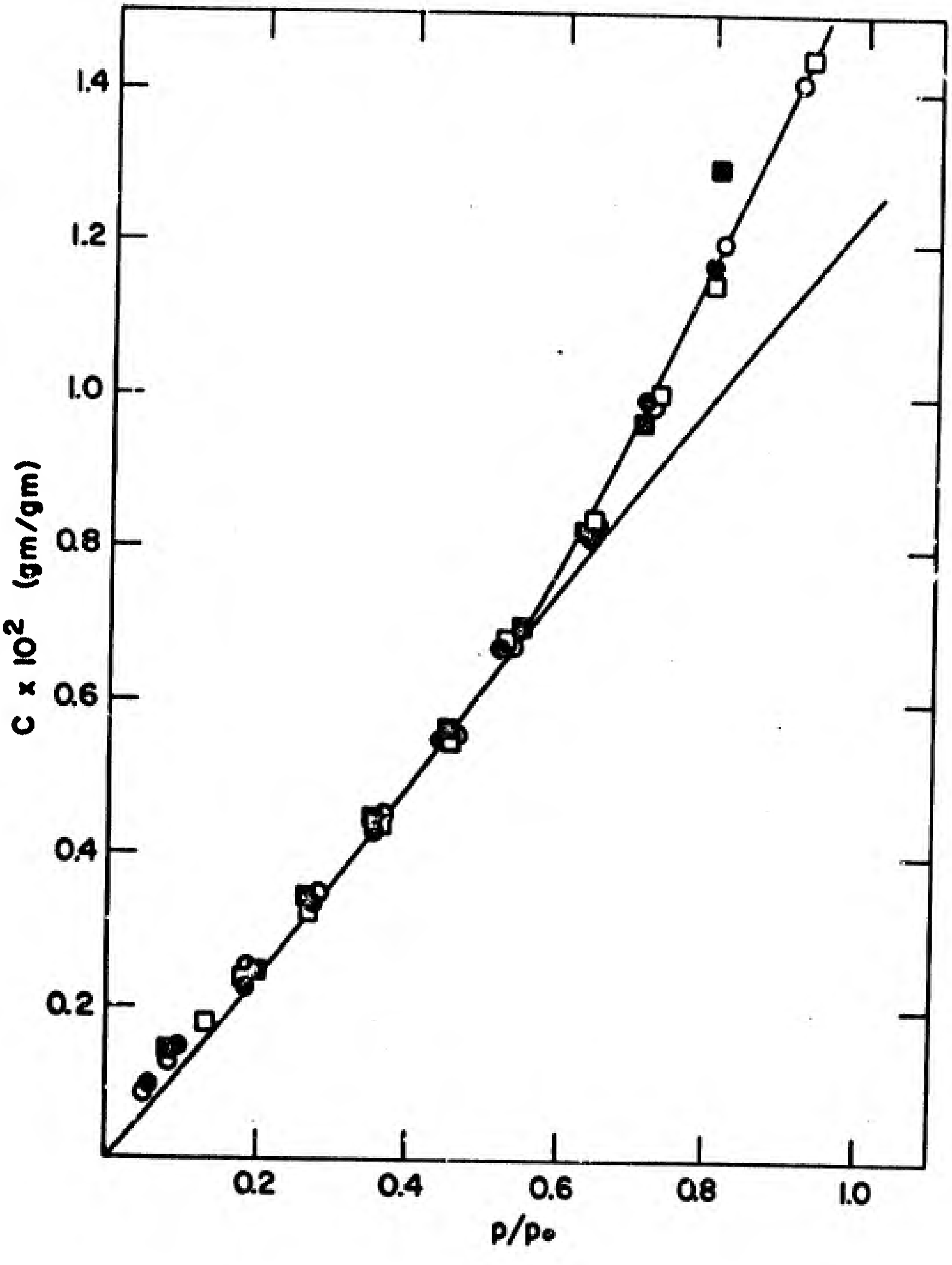

FIGURE 1 Sorption isotherm for poly(butylene adipate) at 40°C; unfilled points sorption, filled points desorption.

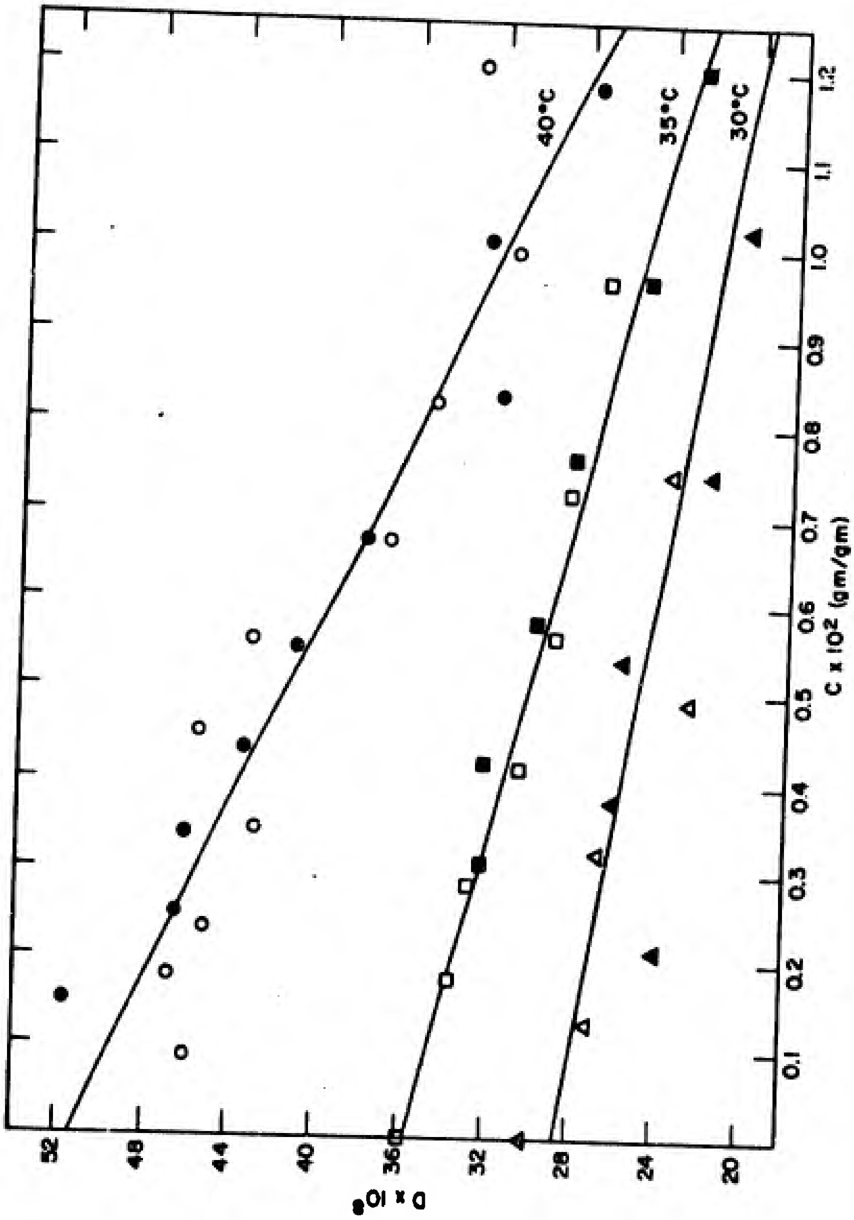

FIGURE 2 Dependence of the diffusion constant for poly(butylene adipate) on water concentration; unfilled points sorption, filled points desorption.

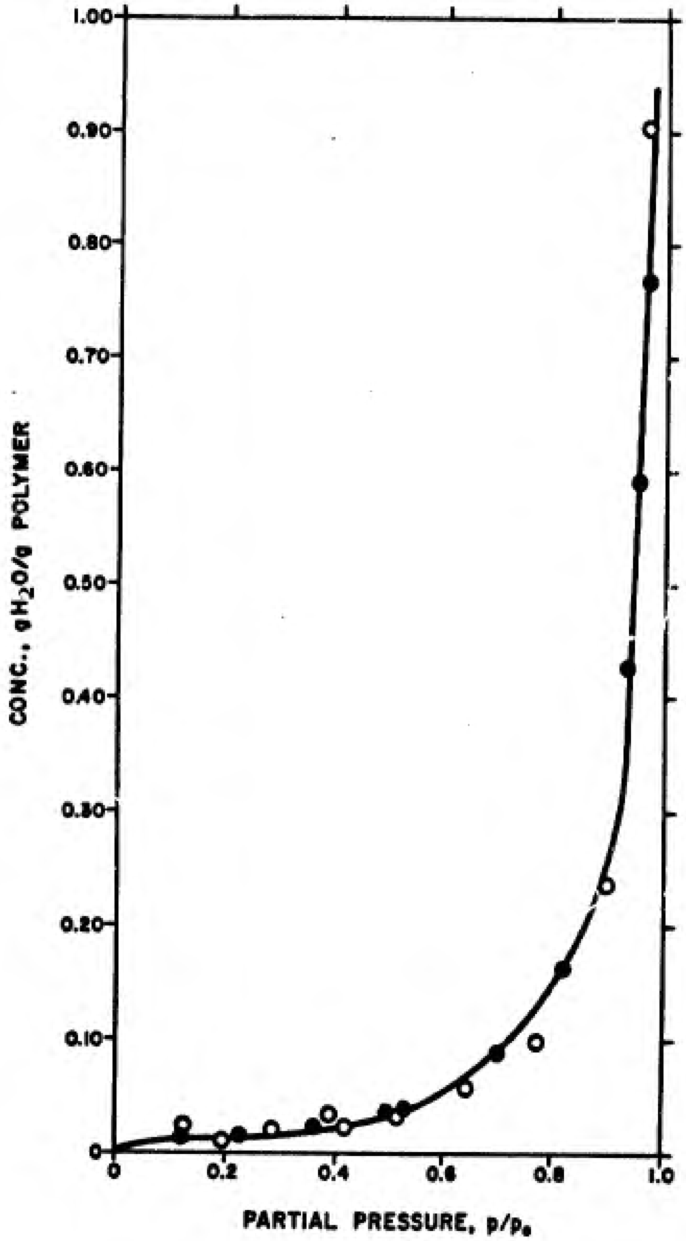

FIGURE 3 Sorption isotherm for poly(ethylene oxide) at 35°C; unfilled points sorption, filled points desorption.

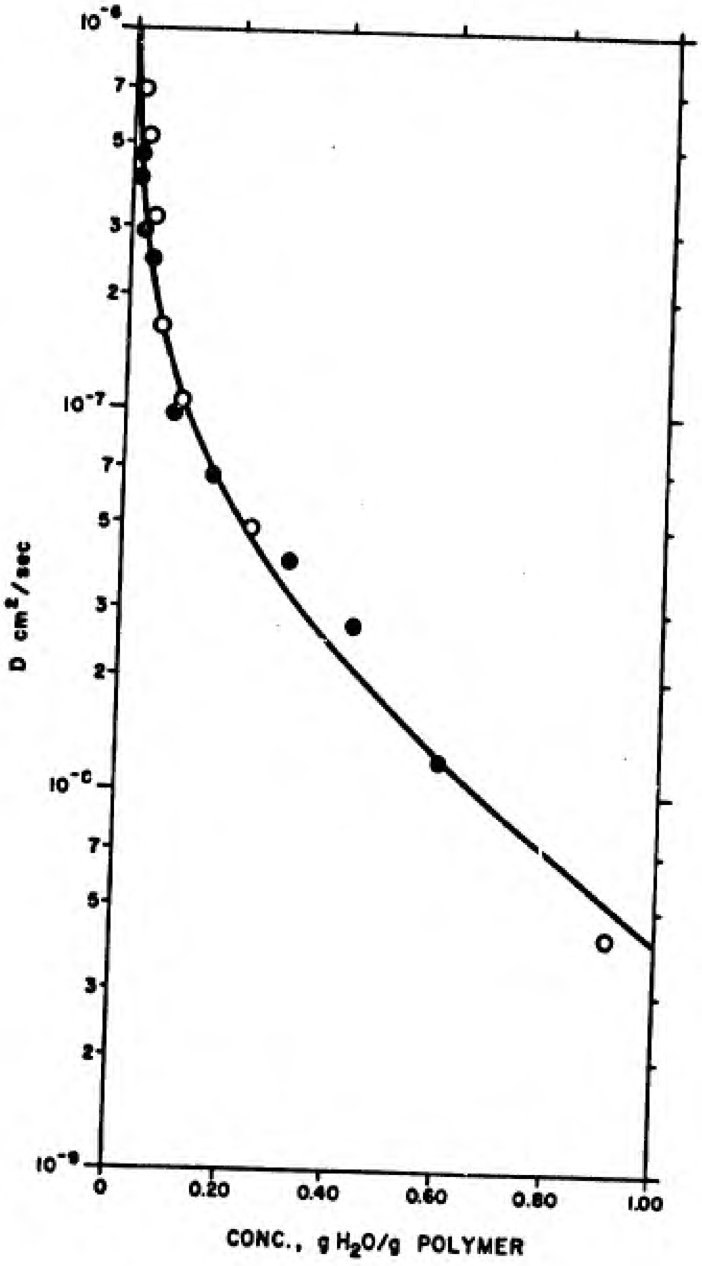

FIGURE 4 Dependence of the diffusion constant for poly(ethylene oxide) on water concentration at 35°C; unfilled points sorption, filled points desorption.