Diffusion of Small Molecules in Semicrystalline Polymers: Water in Polyethylene

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INTRODUCTION

In a previous paper[1] the data in the literature pretaining to the permeation of water vapor through polyethylene have been examined. There it was indicated that, although the agreement between the various values of the permeability coefficient and the activation energy for permeation was not good, certain trends could be established. In an attempt to explain the behavior of the permeability data it was suggested that much of the lack of agreement between the various experimenters could be nominally explained by the postulated existence of microscopic voids in the amorphous portions of the various polymer specimens measured. In the present paper the investigation is extended to include the solubility and diffusion data published for water vapor in polyethylene. It appears that the interpretation of the latter is even more difficult than that of the corresponding permeability data. Only by making bold assumptions in this analysis can any useful conclusions be drawn at all. Accordingly, in the text below, such assumptions have been made where required, and these are indicated. They stem mainly from the very limited number of experimental determinations which are available, and their lack of concordance. Some remarks are also included concerning the general problem of diffusion in semicrystalline polymers.

PUBLISHED SOLUBILITY AND DIFFUSION DATA FOR LOW-DENSITY POLYETHYLENE

The suggestion had been made to the author that variations in the solubility of water between various specimens of polyethylene might be a factor contributing to the wide range of permeability coefficients reported. Obviously if the solubility within the amorphous portion varies from specimen to specimen, the permeability coefficient will vary in the same direction, even though the diffusion coefficient itself may remain constant. In a recent article, McCall, Ambrose, and Lanza[2] have called attention to the fact that the solubility data from three literature sources did not agree. They showed that, with increasing amounts of oxygen incorporated into polyethylene, the solubility of water was enhanced. Thus, in a specimen of low-density polymer which contained 0.6% oxygen by weight, they measured a solubility of 0.10 mg./cm.[3], whereas with unoxidized low- and high-density polymers, they were unable to detect water concentrations as small as 0.05 mg./cm.[3]. They concluded that the higher solubilities measured by others were due to impurities in the specimens examined. Accordingly, one might suppose that, if the diffusion coefficient remained constant but the solubility varied, the latter might give rise to the variations in the permeability coefficient which are observed.

To examine the merit of the suggestion mentioned above, the solubility data from five sources in the literature are presented in Table I including the diffusion and permeability data where available.[2-6] It is apparent that the data do not agree and also that certain trends appear to exist. It is proposed first to discuss the solubility data by themselves.

The solubility data of Table I were determined in three manners. McCall and his associates[2] immersed polyethylene moldings in water and attempted to measure the weight loss of the specimens on drying by using an analytical balance. They were unable to detect a weight loss in those experiments in which unoxidized polymer was used. Rouse,[3] Hauser and McLaren,[5] and Cutler and McLaren[6] used spring balances installed within gas handling systems. By this means the weight of water absorbed by a specimen of polyethylene film in equilibrium with a known vapor pressure of water could be determined by measuring the extension of the spring with a cathetometer. This technique is capable of giving the entire sorption

TABLE I
Permeability, Solubility and Diffusion Data for Low Density Polyethylene

Solubility, mg./cm.^{3}	Permeability coefficient, g. mm./m.^{2}/ day/cm. Hg	Diffusion coefficient cm.^{2}/sec. $\times 10^8$	Solubility technique	Source of data
		Data at 25°C.		
(4.1)	(0.031)	(0.21)^a	spring balance	Rouse (saturation pressure)[3]
0.84	0.015	0.48	time lag	Doty et al.[4]
0.59	0.031	1.44	spring balance	Rouse (extrapolated)[3]
0.18+	0.043	6.74	spring balance	Hauser et al.[5]
<0.05	—	—	analytical balance	McCall et al.[2]
		Data at 40°C.		
1.7	—	—	spring balance	Cutler et al. (saturation pressure)[6]
0.83	—	—	spring balance	Cutler et al. (extrapolated)[6]
0.18	0.086	30.5	spring balance	Hauser et al.[5]

^{a} Corresponds to $\overline{D} = \dfrac{1}{C_0} \displaystyle\int_0^{C_0} D(c)dc$, i.e., integral mean for a concentration-dependent diffusion coefficient.

isotherm as well as the solubility at saturation pressure. Doty, Aiken, and Mark[4] did not make a direct determination of the solubility; rather, they determined the value of the diffusion coefficient from the time required for vapor to diffuse through the specimen. Since the permeability coefficient was also determined in the same experiment, the Henry's Law coefficient could be obtained from the ratio of the permeability coefficient to the diffusion coefficient. The solubility of water in the polymer is obtained by multiplying the Henry's Law coefficient by the vapor pressure of water. This procedure is theoretically exact only if the barrier material is homogeneous. With a partially crystalline barrier, a systematic error appears which causes the diffusion coefficient to be underestimated by perhaps as much as 25%, even though no uncertainty is caused in the solubility value. This will be discussed further on and will not be considered at this point where only the broad trends in the data are being discussed.

Apparently, no determinations of crystalline content are available for any of the polymers of Table I. All that is known about the materials is that they were, no doubt, similar, low-density polymers. Accordingly, one is almost forced to make the simplifying assumption at the outset that important differences in crystallinity did not exist between the specimens used. This is an objectional assumption in some respects, since the solubility can be expected to vary in direct proportion to the amorphous fraction of the polymer, but it is, nevertheless, a useful one for the time. There appears to be no theoretical reason why Henry's

Law should not be obeyed. On the contrary, an argument will be presented further on which will indicate the probable validity of Henry's Law for the polyethylene-water system. It is, therefore, rather remarkable, that the data of Rouse,[3] who gives the sorption isotherm at 25°C., show a pronounced curvature (i.e., concave upwards when concentration is plotted on the y axis and pressure of water vapor on the x axis), indicating a wide deviation from Henry's Law even at moderate pressures. Furthermore, his value for the solubility of water corresponding to the saturation pressure is remarkably high (4.1 mg./cm.^{3}). Examination of the comparable data at 40°C. of Cutler and McLaren[6] reveals a much more logical behavior. In this case, a linear relationship between concentration of dissolved water and pressure of water vapor is obtained for pressures not exceeding 80% of the saturation pressure. If some allowance is made for the experimental error, this linear relation can be extended to 95% of saturation pressure, only the point at 100% humidity not being linearly connected. These considerations suggest that a linear sorption isotherm, extrapolated from the low pressure points to the saturation pressure, might give more reliable values for the solubility than determinations actually made at the saturation pressure. This appears to be the case as Table I shows, where solubility values extrapolated from the low pressure points of Rouse and of Cutler and McLaren agree much better with those of the other experimenters than do the determinations at saturation pressure. Nevertheless, there is not good agreement between the solubility values given by the

various investigators. For ease of comparison, the values in Table I have been listed in order of increasing solubility.

In addition to the solubility values, the corresponding permeability and diffusion coefficients have also been listed. It is obvious that the highest solubilities are not associated with the highest permeabilities. The trends in the permeability coefficients and the diffusion coefficients are in the same direction, whereas the solubility data appear to vary precisely in the opposite direction. The former observation is completely logical, but on the other hand, the only significance which is attached to the latter observation is that the solubility properties and the transport properties are varying independently in the data at hand. There is no reason to expect a precisely inverse relationship *per se.* This is thought to have occurred purely by accident, since only three sets of comparable data are available for examination. The diffusion coefficients increase faster with decreasing solubility than do the permeability coefficients and moreover, vary over a fourteenfold range.

It is important to note that the diffusion coefficient as determined in these experiments is not averaged over crystalline and amorphous phases as is the permeability coefficient, but retains a numerical value characteristic of the amorphous phase as will be shown below. A systematic error, similar to that previously noted, occurs when the ratio of the measured permeability coefficient of a partially crystalline polymer is divided by the Henry's Law coefficient uncorrected for crystalline content to obtain the diffusion coefficient; however, this will later be shown to be only about 25%, likewise, and hence will not affect the reasoning here. Accordingly, these variations in diffusion coefficient tend to indicate definite changes residing within the noncrystalline parts of the polymer. These conclusions cannot be extrapolated very far however, because the data are very sparse. It appears that definitive solubility measurements for water and polyethylene are hard to obtain because of the small magnitude of the property involved.[2] It is apparent, however, that the behavior of the solubility does not explain the permeability behavior, but rather, that the diffusion data reinforce previous conclusions concerning structural effects within the amorphous phase.

PERMEATION, DIFFUSION, AND SOLUBILITY IN PARTIALLY CRYSTALLINE POLYMERS

In the sections which follow it is intended to examine the permeation process in a polymer consisting of a uniform amorphous matrix in which crystalline inclusions are imbedded. Other structural effects such as voids which may possibly occur in either phase are not explicitly considered in this discussion. The main objectives in the succeeding paragraphs are to contrast the diffusion process in semicrystalline and noncrystalline systems and to estimate the errors introduced by the use of formulas developed for homogeneous systems in the former case, as well as to study the role played by solubility parameters.

a. Permeation and Diffusion

Previously a formula, apparently first given by Bent,[7] was used to relate the measured permeability of a partially crystalline polymer P to the permeability of the amorphous phase P_A and the fraction X_A of the polymer by volume which was amorphous, namely:

$$P = P_A X_A \qquad (1)$$

This equation constitutes a statement to the effect that the crystalline portion of the polymer is substantially inactive in the permeation process. It was immediately apparent that this relation was only approximate and that an exact relation would contain parameters describing the geometry of the crystalline regions. In the general case in which the crystalline phase is distributed throughout the polymer one may write:

$$P = P_A X_A \Psi \qquad (2)$$

where $1 > \Psi > 0$

The factor Ψ is a function which describes the reduction of the permeability below the amount $P_A X_A$ due to the distortion of the lines of diffusion flow around the crystallites dispersed throughout the polymer. At high volume fractions of crystalline phase, the amorphous portion exists as a complex network of tortuous narrow channels extending in three dimensions. This channel network will have two obvious characteristics. (*a*) Some of the channels will represent cul-de-sacs which will not be effective in the mass transport process. Other channel segments may be arranged so that they have no component in the direction of flow and moreover have no fugacity gradient for the penetrant in the direction of flow at steady state. (*b*) Few, if any of the channels will span the thickness of the water vapor barrier in a straight line. The consequence of (*a*) is that only a part of the amorphous volume will be active in permeation,

and that of (b) is that the diffusion path will be increased beyond the thickness of the water vapor barrier. Thus, at the higher crystallinities, one can conceive of Ψ as given by:

$$\Psi = \psi_1 \psi_2 \qquad (3)$$

where, by definition, Ψ is the transmission function, ψ_1 is the transport volume fraction (corresponding to (a) above), and ψ_2 is the detour ratio (i.e., the ratio of the thickness of polymer in the nominal direction of diffusion flow to the average length of the diffusion path winding between the crystalline regions). By stipulating that the amorphous portion of the polymer obeys Fick's and Henry's Laws, one can also write:

$$P_A = D_A S_A \qquad (4)$$

where D_A is the diffusion coefficient for water in amorphous polyethylene and S_A is the Henry's Law coefficient for water vapor in amorphous polyethylene. In a sorption experiment, S_A per se is not determined but, instead, a corresponding value S for the composite material. The quantity S is smaller than S_A by a factor X_A, because only the amorphous portion absorbs water, that is:

$$S = S_A X_A \qquad (5)$$

Thus, when one attempts to determine the diffusion coefficient of a semicrystalline material by dividing the permeability coefficient, uncorrected for crystalline content, by the Henry's Law coefficient, also uncorrected for crystalline content, one obtains a quantity:

$$D = \frac{P}{S} = \frac{P_A X_A \Psi}{S_A X_A} = D_A \Psi < D_A \qquad (6)$$

because $0 < \Psi < 1$. This quotient does not equal the diffusion coefficient in the case of a semicrystalline polymer as it does in a completely noncrystalline polymer.

Consider next the determination of the diffusion coefficient from a time lag experiment. In this procedure, a vacuum diffusion apparatus is used, and the penetrant vapor is allowed to diffuse through the polymer film from a reservoir containing penetrant vapor at a fixed high pressure into a reservoir of known volume initially at zero pressure. The rise of pressure in the latter reservoir as a function of time is used to determine the permeability coefficient of the polymer film. Linear extrapolation of the pressure-time curve at steady state to zero pressure gives an intercept on the time axis which may be used to calculate the diffu-

sion coefficient within the film. The mathematical exposition of this method has been given in detail elsewhere for homogeneous films[8] so that it is merely required to modify the treatment where semicrystalline films are concerned.

Imagine a parallelepiped within the polymer. Suppose that its faces of unit area are normal to the nominal direction of diffusion flow which will be taken to be parallel to the y axis. Let the thickness of the parallelepiped be dy. At the face experiencing the highest concentration of penetrant, penetrant will diffuse into the parallelepiped; at the opposing face, penetrant will diffuse out of the parallelepiped. All of that part of the parallelepiped which is amorphous will accumulate penetrant if the former rate exceeds the latter. However, the rate of diffusion will be controlled not by the gradient of the penetrant concentration in the y-direction (as in the homogeneous case) but by the gradient of the penetrant concentration along the average actual length of the diffusion path. Let the variable for this length be ξ. The equation for the material balance in this case becomes:

$$X_A \left(\frac{\partial C}{\partial t} \right) dy = D_A X_A \psi_1 \left(\frac{\partial^2 C}{\partial \xi^2} \right) d\xi \qquad (7)$$

where C is the penetrant concentration in the amorphous portion, t is time, and the other symbols have been defined previously. Rearranging the terms and making the identification: $d\xi/dy = 1/\psi_2$, one obtains Poisson's equation in the form:

$$\frac{\partial C}{\partial t} = \frac{D_A \psi_1}{\psi_2} \left(\frac{\partial^2 C}{\partial \xi^2} \right) \qquad (8)$$

If the thickness of the polymeric vapor barrier is L and the average actual length of the diffusion path is $\theta (= L/\psi_2)$, a direct comparison with the equations for the time-lag experiment on homogeneous films[8] indicates that the solution of eq. (8) will be:

$$t_0 = \frac{\theta^2}{6 D_A \left(\dfrac{\psi_1}{\psi_2} \right)} = \frac{L^2}{6 D_A \psi_1 \psi_2} \qquad (9)$$

where t_0 is the time lag (i.e., intercept).

Since t_0 and L are measured quantities, the effective diffusion coefficient which is determined by eq. (9) is that given by eq. (6). It follows directly that dividing D obtained from a time lag experiment into the measured permeability gives an accurate estimate of the Henry's Law coefficient S. It is apparent, however, that the simple relations used to describe homogeneous (completely non-

crystalline polymers) systems are not really adequate for the description of permeation through semicrystalline polymers. Even so, it appears that, irrespective of the systematic error introduced on this account, all the diffusion data in Table I are similarly affected and hence are strictly comparable.

b. Transmission Functions for Permeation and Diffusion

It should be possible to calculate the transmission function by means of equations given for the computation of the specific electrical conductivity of a heterogeneous conductor. If the permeability equation is formulated in terms of the fugacity of the penetrant instead of the external pressure, it is immediately apparent that the analogy to the electrical case is exact. Thus, the fugacity of the penetrant becomes the analog of the electrical potential, the diffusion flow becomes the analog of the current density, and the permeability coefficient becomes the analog of the specific conductivity. Both sets of variables obey the Laplace equation at steady state, and the conditions of continuity at the phase boundaries correspond exactly. Maxwell[9] has presented an equation which expresses the electrical conductivity of a heterogeneous conductor in which the included phase is present as identical spheres randomly imbedded in a matrix phase. Thereby the conductivity of the composite material is expressed in terms of the conductivities of both phases and the volume fraction of either phase. Such an equation
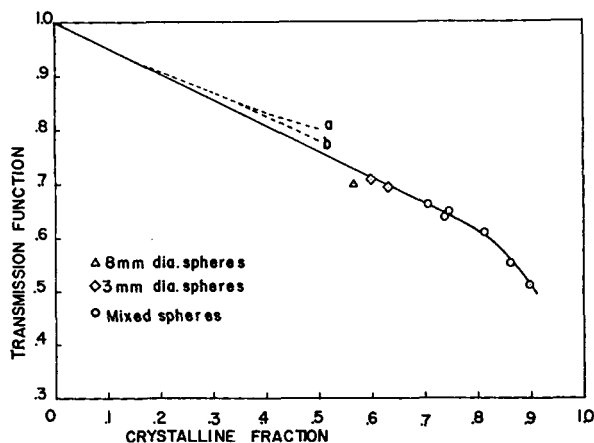
would be particularly appropriate, because polymer crystals generally occur as spherulites within the amorphous matrix. In terms of Maxwell's equation, the transmission function becomes:

$$\Psi = \frac{2}{3 - X_A} \qquad (10)$$

This equation is necessarily approximate because it is valid only when the spherical inclusions are sufficiently far apart so that they affect the diffusion flow only in their respective, immediate neighborhoods. This condition is violated to an increasing extent at volume fractions of crystalline phase exceeding 0.3. Runge[10] has reexamined this problem and has provided a more rigorous solution which does not fail seriously until the volume fraction of crystallinity reaches a value of $\pi/6$. The solution of Runge has the form

$$\Psi = \frac{1}{X_A}\left[1 - \frac{3X_C}{2 + X_C - 0.392X_C^{10/3}}\right] \quad (11)$$

where X_C is the volume fraction of polymer which is crystalline. The transmission functions as computed by means of the equations of Maxwell and of Runge are shown as dotted lines in Figure 1, where they are compared with an empirically determined transmission function which will now be discussed.

Having established the validity of the electrical analog treatment for the computation of transmission functions, the next obvious step is to employ the electrical analog to determine the transmission function from conductivity measurements. In the simplest type of experiment, a collection of glass balls would be immersed in a salt solution, and the electrical conductivity of the salt solution-glass ball mixture would be compared with that of the salt solution alone. If the fraction of the total volume occupied by the balls were also known, the transmission function could be simply calculated from the relation:

$$\Psi = \frac{\rho_{SB}}{\rho_S(1 - X_B)} \qquad (12)$$

where ρ_S is the specific conductivity of the salt solution, ρ_{SB} is the specific conductivity of the salt solution-glass ball mixture, and X_B is the volume fraction of mixture occupied by the glass balls. This experiment has the advantage over the previous procedures that, by employing random packing techniques for the glass balls and by mixing

Fig. 1. Plot of the transmission function (Ψ) vs. the volume fraction of polymer which is crystalline X_C: (a) calculated with Maxwell's equation; (b) calculated with Runge's equation; (———) empirically determined transmission function.

balls of various sizes in varying proportions, a range of packing fractions (corresponding to X_C in the polymer case) can be obtained, all of which lie in the region (of X_C) for which computed values of Ψ cannot be obtained. Nine such values, calculated from experiments in the literature[11] are plotted in Figure 1. These experimental values cover the range of crystallinities from about 55% to 90%, as shown in Table II. The empirical transmission

TABLE II
Transmission Functions Determined by Electrical Conductivity Measurements on Model Systems[11]

Volume fraction conducting phase X_A	Volume fraction inclusions X_C	Transmission function Ψ
0.435	0.565	0.699
0.402	0.598	0.709
0.368	0.632	0.694
0.294	0.706	0.662
0.262	0.738	0.637
0.254	0.746	0.649
0.187	0.813	0.610
0.139	0.861	0.552
0.102	0.898	0.510

function curve was drawn linearly from the point $X_C = 0$, $\Psi = 1$, close to the calculated curves, and joined smoothly onto the almost hyperbolic curve drawn through the experimental points. Although there are no experimental points in the linear region, there can be little doubt that the path of the true curve lies close to the empirical curve. It is apparent immediately that the first approximation curve of Maxwell's equation and the second approximation curve of Runge's equation approach the empirical curve almost asymptotically as X_C approaches zero, and that they become coincident at $X_C = 0$. The equation of Runge approximates the empirical curve better than does Maxwell's equation, in that it deviates less from the latter and also because it is more nearly linear.

One can now define the relative permeability of a semicrystalline polymer as the ratio of the permeability of the whole polymer, P, to that of its amorphous phase, P_A. The transmission function-crystallinity relation being known, it becomes possible to calculate the relative permeability as a function of the amorphous (or crystalline) volume fraction merely by multiplying the amorphous fraction by the corresponding value of the transmission function thus:
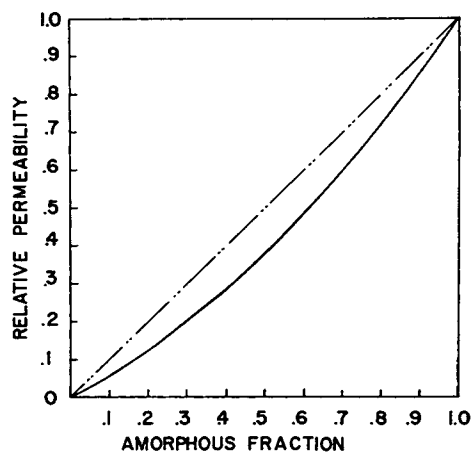
$$P/P_A = X_A \Psi(X_A) \qquad (13)$$

Fig. 2. Plot of the relative permeability P/P_A vs. the volume fraction of polymer which is amorphous X_A. Broken straight line is given for comparison.
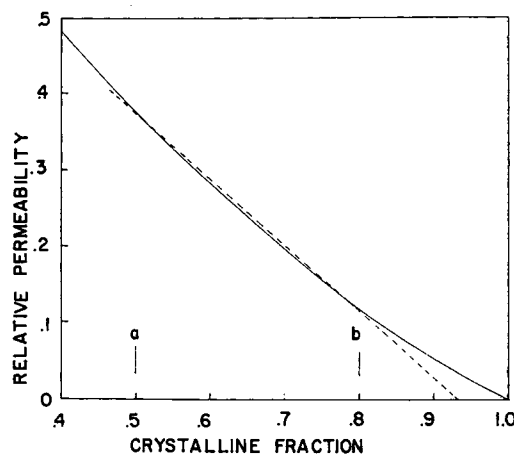

Fig. 3. Plot of the relative permeability P/P_A at intermediate to high crystallinities as a function of the volume fraction X_C of crystalline polymer. Dashed straight line is given for comparison. Indices a and b span the range of crystallinities most probably encountered in reference 1.

The results of this multiplication, which are plotted in Figure 2, are precisely what one would expect. It is particularly interesting to examine this curve in detail in the region of high crystallinity, i.e., low X_A, which is the region of technological importance. This has been done in Figure 3, in which the region from 40% crystallinity to 100% crystallinity (X_A from 0.6 to 0) is expanded. One observes that although the computed relative permeability relation is concave upwards in this region, the curvature becomes virtually zero between 50 and 80% crystallinity (X_A between 0.2 and 0.5). The similarity of this figure and Figure 4 of the previous paper[1] is striking. In the latter it was shown that, provided the measured permea-

bilities in the literature were corrected for the bias between experimenters (postulated to be due to varying quantities of microvoids in the various polymer series measured), a very linear relation exists between permeability and density (i.e., crystallinity) in the region of intermediate to high crystallinity. Although various methods of determining the crystallinity do not agree completely, it is indicated by the calculation of Myers[12] et al. that most probably these specimens were between 55 and 80% crystalline. This is precisely the range of crystallinities in which the relative permeability function is the most nearly linear; thus the linear relation found experimentally is explained.

In the experimental permeability-density curves of Figure 3 in the previous study,[1] the linear functions appear to extrapolate to a density of 0.973. On the basis of the specific volume data provided by Bueche[13] a volume-fraction crystallinity of about 88% is calculated. If a straight line is drawn parallel to the dotted line of Figure 3 but tangent to the calculated curve, an extrapolated volume fraction crystallinity of 92% is obtained. In view of the uncertainties in the experimental data, this is considered very good agreement.

In the region between 90 and 100% crystallinity, the transmission function is changing rapidly, and the curve is not available. It is not likely that this function will go to zero, but it will continue to decrease. Not withstanding this uncertainty, the relative permeability function can easily be extrapolated to 100% crystallinity because the smallness of X_A in this region very strongly damps the rapid change in Ψ. Table III lists the values of the transmission function and of the relative permeability used in this work.

c. The Sensitivity of the Transmission Function to Changes in the Geometry of the Crystalline Regions

It remains to discuss the effect of reasonable changes in the geometry of the crystalline regions and to show, if possible that these changes will not be important. Because of the inherent complexity of the problem, this can be demonstrated only by implication. Thus, in the calculation given by Runge as applied to the present problem, the spherulites, which may not be absolutely crystalline themselves, are replaced by identical, impenetrable spheres arranged in a simple cubic lattice. The empirical curve lies really quite close to the curve of Runge, which is coincident at its upper end with that of Maxwell's. Since Maxwell's curve was determined for assemblies of identical spheres in random packing, these calculated curves do not seem to be very sensitive to the mode of packing in the region in which both are valid. No singularities are encountered as one progresses down the empirical curve into the region of mixtures of spheres of different radii in a dense but random packing. In the corresponding conductivity experiments, the sphere diameters ranged from over 3 mm. to those of fine sand. From this one would conclude that neither a wide distribution of sphere diameters nor relatively dense packing has any unusual effect upon the transmission function.

The effect of departures from sphericity can be discussed on a slightly different basis. It is known that, when polyethylene and similar regular polymers crystallize in the presence of pronounced anisotropic stresses, oriented crystalline regions are formed which are distinctly different from spherulites.[14] In the case of extruded films, these crystalline regions appear to be acicular, with the major axes oriented in a preferred direction in the plane of the sheet. The orientation is not complete, and, in fact, a distribution of angles between the direction of orientation and the major axes of the crystalline regions always exists. In the plane normal to the direction of orientation, the distribution of the projections of the major axes is angularly symmetrical. In drawn fibers, a far more pronounced orientation of the crystalline regions appears in which the crystalline regions are strongly oriented parallel to the fiber axis.

TABLE III
Transmission Functions and Relative Permeabilities for
Semicrystalline Polymers

Volume fraction amorphous X_A	Volume fraction crystalline X_C	Transmission function Ψ	Relative permeability P/P_A
1.00	0.00	1.000	1.000
0.90	0.10	0.952	0.857
0.80	0.20	0.904	0.723
0.70	0.30	0.856	0.599
0.60	0.40	0.808	0.485
0.50	0.50	0.760	0.380
0.45	0.55	0.735	0.331
0.40	0.60	0.712	0.285
0.35	0.65	0.688	0.241
0.30	0.70	0.665	0.200
0.25	0.75	0.640	0.160
0.20	0.80	0.613	0.123
0.15	0.85	0.570	0.086
0.10	0.90	0.510	0.051
0.00	1.00	---	0.000

A mathematical model of a geometry for a crystalline phase, more extremely oriented than either of these actual conditions, would be one in which the spherulites were completely distorted into uniform cylinders arranged parallel to each other and normal to the diffusion flow. For this geometry, Runge[10] gives an equation, in terms of which the transmission function becomes:

$$\Psi_{cyl} = \frac{1}{X_A} \left[1 - \frac{2X_C}{1 + X_C - 0.306X_C^4} \right] \quad (14)$$

This equation can be used to compare the behavior of the cylindrical geometry with that of the spherical geometry described by eq. (11). Thus at $X_A = X_C = 0.5$, $\Psi_{spher} = 0.780$, whereas $\Psi_{cyl} = 0.648$, and between these two values there is only 18.5% difference. When it is emphasized that this 18.5% represents the difference between a spherical geometry and a cylindrical geometry which is only remotely approached in the cases of interest here, it immediately follows that the transmission function is virtually insensitive to the variations in the geometry of the crystalline regions which could be reasonably expected to exist in fabricated polyethylene, with the possible exception of cold-drawn fibers.

d. Theoretical Solubility of Water in Polyethylene

It is appropriate at this point to examine the solubility of water in polyethylene from a less empirical point of view. In view of the fact that the amorphous phase of polyethylene is well above its glass transition temperature at 25°C., its molecular architecture should be very nearly that of a liquid aliphatic hydrocarbon. The possibility should exist, therefore, that one might calculate the solubility of water in the amorphous phase from solubility data obtained upon the lower hydrocarbons. In the latter case, solubilities can be determined in the liquid phase with high precision by using water containing radioactive hydrogen. Such data have been determined by Black et al.[15] and have been successfully correlated by Hildebrand and Scott, who write:[16]

$$\ln a_2 = \ln \phi_2 + \phi_1 \left(1 - \frac{V_2}{V_1} \right) + \frac{V_2\phi_1^2(\delta_2 - \delta_1)^2}{RT}$$

$$(15)$$

where a_2 is the activity of water in the solution ϕ_1, ϕ_2 are the volume fractions of hydrocarbon and water, respectively, in the solution; V_1, V_2 are the molar volumes of hydrocarbon and water, respectively; δ_1, δ_2 are solubility parameters for the hydrocarbon and water, respectively; R is the gas constant, and T is the absolute temperature. It is important to observe that in the development of this formula, a lattice calculation has been made for the entropy of solution to correct for the disparity in the molecular sizes of water and hydrocarbon. Flory[17] has successfully used precisely this treatment with high polymers and penetrants and has shown that in the limit of low concentrations of penetrant this formula requires that Henry's law be obeyed. On this basis, curved sorption isotherms become questionable. When equilibrium is established between the water and the hydrocarbon, $\ln a_2 = 0$, and $\phi_1 \cong 1$. Further, $V_2/V_1 \cong 0$ if polyethylene is the hydrocarbon, and eq. (14) becomes:

$$-\ln \phi_2 = 1 + \frac{V_2(\delta_2 - \delta_1)^2}{RT} \quad (16)$$

where $V_2 = 18$ cm.[3], $R = 1.987$ cal./°K./mole, and $T = 298$°K. The solubility parameter for the hydrocarbon δ_1 is equal to the square root of the cohesive energy density, and this latter quantity is equal, for the hydrocarbon, to its energy of vaporization divided by its molar volume. In the limit of infinite molecular weight, the cohesive energy density for amorphous polyethylene should approach the ratio of the increment of the heat of vaporization per methylene group to the increment of molar volume per methylene group. For the former quantity, Billmeyer[18] gives the value 1.169 kcal./mole, and for the latter Glasstone[19] gives 22.0 cm.[3]. Thus the cohesive energy density becomes 53.1 cal./cm.[3], and the solubility parameter δ_1 becomes 7.3 cal.[1/2]/cm.[3/2]. This is, in some respects, a rather theoretical value because the heat of vaporization of polyethylene cannot, of course, be measured. It is possible to obtain an empirical value for δ_1 from measurements of the amount of swelling of the polymer caused by a variety of solvents, the solubility parameters of which are known. In this way Richards[20] has adduced a value of $\delta_1 = 7.9$ for polyethylene. This is significantly higher than the theoretical value, a circumstance by no means unusual in solubility experiments. The greater emphasis at this time will be placed upon the theoretical value ($\delta_1 = 7.3$), because this corresponds with the fact that, in the use of Hildebrand's expression, the theoretical solubility parameters for the hydrocarbons had been used to determine the empirical parameter for water. Although consistency requires the use of the theoreti-

cal δ_1, the conclusions would be little changed if the empirical value were used instead.

The solubility parameter for water δ_2, cannot be estimated from heats of vaporization because of the complex interactions existing between water molecules. However, by using empirical values of δ_2 which are, in fact, of the same order of magnitude as that calculated from the energy of vaporization, it is possible to reproduce the solubility data for various hydrocarbon series. Thus, for saturated aliphatic hydrocarbons, $\delta_2 = 24.0$, whereas for monoolefins a value of 22.5 is appropriate. Since polyethylene contains relatively little unsaturation, the former value will be used. The results of this calculation are given in Table IV. It is immediately apparent that, if polyethylene behaves as a saturated aliphatic hydrocarbon, the solubility can be expected to be less than the minimum amount detectable by McCall et al. Thus, their conclusion that impurities in the polyethylene specimens of other experimenters account for the higher solubilities observed is well taken. Actually, the calculated solubility is a sensitive function of δ_2, and if values of δ_2 equal to 23.3 and 22.5 are arbitrarily substituted in the calculation, δ_1 remaining constant, solubilities of 0.06 and 0.13 mg./cm.³, respectively, are obtained. The latter value corresponds to the solubility expected if the polymer behaved as a monoolefin. Although polyethylene contains a very small amount of unsaturation, this is probably not enough to cause it to resemble an olefin. However, because polyethylene is sometimes fabricated at high temperatures in the presence of atmospheric oxygen, the resulting polymers may contain oxygenated structures, more polarizable than double bonds in amounts depending upon their thermal history and formulation. Accordingly, measured solubilities in the range of 0.2 to 0.8 mg./cm.³ do not appear unreasonable for a slightly oxidized polymer. The high values of Rouse (4.1 mg./cm.³) and Cutler and McLaren (1.7 mg./cm.³) are still

open to question. It is also evident that this line of reasoning would indicate a fourfold variation in solubility could occur and that, if this happened with the diffusion coefficient remaining constant, the wide spread of permeability values reported in the literature could be nominally explained, without postulating structural effects such as microvoids. However the inadequacies of such an argument have been detailed in a previous section.

Equation (15) which was used in the previous calculation is, of course, an expression for $\overline{\Delta F_2}/RT$ where $\overline{\Delta F_2}$ is the partial molal free energy change for the penetrant in going from pure liquid to the solution in the polymer. The first two terms on the right-hand side of eq. (15) give, to a certain approximation, $-\overline{\Delta S_2}/R$, where $\overline{\Delta S_2}$ is the corresponding partial molal entropy. The third term gives $\overline{\Delta H_2}/RT$, where $\overline{\Delta H_2}$ is the partial molal heat of solution (approximately). Thus, with sufficient accuracy for the present discussion one may write:

$$\overline{\Delta H_2} \cong V_2(\delta_2 - \delta_1)^2 \qquad (17)$$

On the basis of the numerical values of the parameters as given in eq. (16) and Table IV, a value of 5.0 kcal./mole is obtained for $\overline{\Delta H_2}$. This high value corresponds with low affinity of polyethylene for water, and it has previously been used to obtain a reasonable estimate of the energy of activation for the diffusion of water vapor in polyethylene.[1]

CONCLUSIONS

In the present report attention has been focused upon the solubility parameters and the diffusion coefficients of the polyethylene-water system in the hope that by a study of these quantities some explanation would be found for the lack of agreement in the published permeability data. Some consideration was also given to the systematic errors which are introduced into the discussion when the simple formulas developed for homogeneous media are applied to nonhomogeneous media. In the first activity it was shown that solubility and diffusion data disagree even more than do the permeability data. The disagreement is so severe that the systematic errors introduced by the use of formulas for homogeneous media are unimportant, although they are nonetheless real and would be of importance if agreement were achieved in other respects. In the second activity, the empirical transmission function has been obtained without the use of permeability data or adjustable constants. The success of this function in deriving the linear per-

TABLE IV
Calculated Solubility of Water in Low Density Polyethylene

Solubility parameter for polyethylene δ_1, cal.$^{1/2}$/cm.$^{3/2}$	7.3[a]
Solubility parameter for water δ_2, cal.$^{1/2}$/cm.$^{3/2}$	24.0
Volume fraction water in amorphous phase ϕ_2	0.77×10^{-4}
Solubility of water in 40% amorphous polyethylene, mg./cm.³	0.03

[a] If the empirical value, $\delta_1 = 7.9$ had been used, a solubility of 0.056 mg./cm.³ would have been obtained.

meability-crystallinity function previously found for the range of technically important crystallinities is strong evidence for the validity of this approach. By the same token, the fact that this function is insensitive to reasonable geometric variations and because it appears in the expressions for the effective diffusion coefficients in the same way in both the procedures used in the study of permeation of water vapor through polyethylene, it cannot be used to explain the variable permeability and diffusion coefficients recorded in the literature. A comparison of the linear density-permeability functions determined with conventional polymers, intermediate density polymers, and high density polymers with the spread of permeability values reported for conventional polyethylene indicates that the gradient of this function is insufficient to provide an explanation of this spread based upon reasonable variations in crystallinity alone. Another important conclusion that can be drawn from the totality of data is that, although solubility variations may exist among specimens of polyethylene, such variations will not account for the variations in permeability which are observed. Instead, it appears that even more manifest variations in the diffusion coefficient are the root of the trouble, and this reinforces the original postulate that significant differences exist in the amorphous portions of the various specimens of polyethylene. In connection with the structure of the amorphous portion of polyethylene, it can now be reported that Bettelheim and Stein[21] have recently presented conclusive evidence for the existence of microvoids in drawn polyethylene fibers and that Reding[22] has demonstrated the existence of appreciable void fractions in molded high density polyethylene articles. Thus one possibility which cannot yet be ruled out is that related structural anomalies are causing the variable behavior of conventional polyethylene films. Since the commercial manufacture of polyethylene films is now accomplished by rather complicated mass production techniques, it is likely that the structure of the amorphous phase could be significantly influenced by the process variables. It is currently the practice to incorporate additives (i.e., antioxidants, slip and antiblocking agents, and modifiers) into polyethylene to assist in processing. The effect of these materials upon the water vapor transport properties of this polymer does not appear to have been separately investigated and has necessarily been ignored in the analysis just given because there was no explicit mention of such additives being present in the experiments just discussed.

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Synopsis

Published data on the solubility properties and diffusion coefficients for water in polyethylene are critically examined and related to the permeability coefficients analyzed in a previous paper. The data examined in the present article are even more variable than the permeability data, the measured diffusion coefficients varying over a fourteenfold range. Solubilities vary less from specimen to specimen but do so in an order opposite to that of the diffusion coefficients. Accordingly the permeability coefficients vary much less than do the diffusion coefficients. In an examination of the permeation process, as it must occur through semicrystalline polymer films, it is demonstrated that a systematic error is introduced if permeation through such films is described by means of equations developed for homogeneous materials.

The error has been evaluated by means of an electrical ana-
log and equations describing diffusion in semicrystalline
polymers are derived which complement those already in
existence for diffusion in homogeneous polymers. By means
of these equations it is shown that the variations in permea-
bility and diffusion coefficients cannot be explained on the
basis of reasonable variations in the amount of crystallinity
between otherwise comparable polymers or by reasonable
variations in the way in which the crystalline regions occur
in the amorphous matrix. The conclusion previously
reached to the effect that variations in the structure of the
amorphous phase from specimen to specimen are respon-
sible for irreproducible transport properties still appears
valid.

Résumé

Les données relatives aux propriétés de solubilité et coef-
ficients de diffusion de l'eau dans le polyéthylène sont exam-
inées critiquement et reliées aux coefficients de perméabilité
analysés dans un article précédent. Les résultats examinés
ici sont même plus variables que les données de perméabilité,
les coefficients de diffusion mesurés variant sur une gamme
de quatorze fois leur valeur. Les solubilités varient moins
d'un échantillon à un autre mais en sens inverse de celui des
coefficients de diffusion. Conséquemment les coefficients
de perméabilité varient beaucoup moins que les coefficients
de diffusion. En examinant le processus de perméation, au
sein de films polymériques semicristallins, en introduit une
erreur systématique si la perméation à travers de tels films
est décrite au moyen d'équation développées à l'intention de
matériaux homogènes. Cette erreur a été évaluée au moyen
d'un analogue électrique, et des équation de diffusion au sein
de polymères semicristallins ont été dérivées; elles complè-
tent celles qui existent déjà pour la diffusion dans les poly-
mères homogènes. Au moyen de ces équations on montre
que les variations de perméabilité et de coefficients de dif-
fusion ne peuvent être expliquées sur la base de variations
raisonnables du taux de cristallinité entre des polymères
comparables ou de variations raisonnables dans la façon sui-
vant laquelle les régions cristallins se présentent dans un
matériau amorphe. La conclusion précédemment établie
semble valable, à savoir que les variations de structure de
phase amorphe d'un échantillon à l'autre sont responsables
des propriétés irreproductibles.

Zusammenfassung

Die Literaturangaben für die Löslichkeitseigenschaften
und Diffusionskoeffizienten von Wasser in Polyäthylen
werden kritisch überprüft und zu den in einer früheren
Veröffentlichung behandelten Permeationskoeffizienten in
Beziehung gesetzt. Die Zahlen, die in der vorliegenden
Arbeit aufscheinen, zeigen noch grössere Unterschiede als
die auf die Permeabilität bezüglichen, da die gemessenen
Diffusionskoeffizienten über einen vierzehnfachen Bereich
variieren. Die Löslichkeiten ändern sich von Probe zu
Probe weniger stark und ihre Änderung verläuft im entge-
gengesetzten Sinne zu der der Diffusionskoeffizienten. In
Übereinstimmung damit sind die Änderungen der Permea-
bilitätskoeffizienten viel weniger stark als die der Diffusions-
koeffizienten. Bei einer Analyse des Permeationsvorganges,
wir er in semikristallinen Polymerfilmen stattfinden muss,
wird gezeigt, dass bei der Beschreibung der Permeation
durch solche Filme mittels der Gleichungen die für homogene
Materialien entwickelt wurden, ein systematischer Fehler
eingeführt wird. Dieser Fehler wurde durch ein elektrisches
Analogon bestimmt und es werden Gleichungen zur Besch-
reibung der Diffusion in semikristallinen Polymeren abgelei-
tet, welche die für die Diffusion in homogenen Polymeren
schon vorhandenen ergänzen. An Hand dieser Gleichungen
wird gezeigt, dass die Änderungen der Permeabilitäts- und
Diffusionskoeffizienten weder auf Grundlage einer plausiblen
Änderung der Grösse des kristallinen Anteils bei sonst ver-
gleichbaren Polymeren noch durch plausible Änderungen
der Anordnung der kristallinen Bereiche in der amorphen
Matrix erklärt werden kann. Der schon früher gezogene
Schluss, dass nämlich Änderungen in der Struktur der
amorphen Phase von Probe zu Probe für die Nichtreprodu-
zierbarkeit der Transporteigenschaften verantwortlich sind,
muss immer noch als gültig betrachtet werden.