

Diffusion Coefficients of Liquids in Polymer Membranes by a Desorption Method

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Synopsis

A method to obtain the diffusion coefficients and free volume parameters from desorption data for organic liquids in polymer films is presented. The method consists of fitting a numerical solution of the diffusion equation to experimental desorption data. Some problems that arise in the solution of the diffusion equation are discussed and results for a benzene-polyethylene system are presented.

INTRODUCTION

It is well known in the literature that the diffusion coefficients in polymers of gases or liquids which interact and swell the polymer are functions of the concentration of the diffusing molecules. The use of time-lag or permeation experiments yields only the concentration-average diffusion coefficients. For certain analysis, it is desirable to obtain the diffusion coefficient and its functional relationship with the concentration of the diffusing molecules in the polymer. One method by which it is possible to obtain the diffusion coefficient-concentration dependence is by the analysis of absorption data. Crank^{1,2} describes several methods to perform this analysis.

An alternate way to obtain the concentration dependence of the diffusion coefficient is based on the use of desorption data. McCall³ has developed a numerical procedure to analyze desorption data. However, his procedure is limited to cases where the diffusion coefficient can be integrated analytically with respect to concentration. The free volume theory of diffusion⁴ has been extended to polymeric systems by Fujita.⁵ It provides a fairly reasonable explanation of the concentration dependence of the diffusion coefficient. The basic idea in the free volume approach is that the mobilities of both the polymer segment and the diffusing molecule in a polymer-diluent system are primarily determined by the amount of free volume present in the system.

The purpose of the present study is to develop a method based on desorption data, in order to obtain the diffusion coefficient and its concentra-

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tion dependence when this relationship cannot be integrated analytically. This method consists of fitting a numerical solution of the diffusion equation to experimental data and the application of the free volume theory of diffusion to estimate free volume parameters. Numerical procedures and results for the system benzene–polyethylene are presented.

THEORY

Diffusion Equation

The diffusion equation will now be set up for the diffusion of a substance through a polymer sheet. As the area of the face is much greater than that of the edges, diffusion normal to the edges will be neglected. The equation will be developed taking into account the fact that the polymer sheet swells with the addition of the penetrant. The nomenclature will be that used by Bird et al.⁶

Fick's law of diffusion is

$$j_a = -\rho D_{ab} \nabla \omega_a \quad (1)$$

where j_a is the mass flux of component a relative to the mass average velocity v ; ρ is the density of the system; ω_a is the mass fraction of component a ; ∇ is the del operator, in this case $\partial/\partial x$ since other derivatives are neglected for the case of a "thin" sheet.

By writing the diffusion equation with respect to an axis which moves with the polymer component, and doing a mass balance, the following is obtained:

$$\frac{\partial \rho_a}{\partial t} = \frac{\partial}{\partial x} \left[\rho \frac{D_{ab}}{\omega_b} \frac{\partial \omega_a}{\partial x} \right] \quad (2)$$

where ρ_a is the concentration of component a , per unit volume of the system; t is time; x is the distance along which diffusion takes place; and D_{ab} is the diffusion coefficient of a with respect to b .

Up to now, the equation is general, the only assumption being that there is no diffusion in the y and z directions (through the edges). However, in its present form, the diffusion equation cannot be solved because of the presence of the density term ρ . This term is a function of x because of the fact that the polymer swells when penetrant dissolves and contracts when penetrant diffuses out. At zero concentration, the density is that of the pure polymer, but upon absorption of a liquid, the density will change. Thus, information is required about the density change with composition of the system. With the systems studied, this information is difficult to obtain, and in its absence it will be assumed that the volumes of the penetrant a and the polymer b are additive. This assumption is a good one for many polymer–liquid systems. For example, McCall and Slichter⁷ report for polyethylene a solubility and swelling factor in n -hexane of 12.6 wt-% and 14%, respectively, and in benzene of 17.2 wt-% and 16%, re-

spectively. With their data and the assumption of additive volume, a swelling factor for *n*-hexane and benzene can be calculated as 16% and 18%, respectively, which is close to the experimental values. Bent and Pinsky⁸ report a comparison between the additive volume assumption and the per cent increase in volume actually measured for numerous organic liquid-polyethylene systems. Their data indicate that the assumption is fairly accurate. For example, at 70°F with benzene, the additive volume calculation yields a 16% increase in volume, whereas the experimental values range from 15.2%–17.2%.

Mathematically, the additive volume assumption can be expressed as

$$V_t = (\text{mass of } A) \times V_a^0 + (\text{mass of } B) \times V_b^0 \quad (3)$$

where V_t is the total volume of the system; and V_a^0 , V_b^0 are the specific volumes of pure *A* and *B*, respectively. With this assumption, the diffusion equation, eq. (2), can be written as

$$\frac{\partial \rho_a}{\partial t} = \frac{\partial}{\partial x} \left[\frac{D_{ab}}{(1 - v_p)} \frac{\partial \rho_a}{\partial x} \right]. \quad (4)$$

In more familiar notation this is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(\frac{D_{ab}}{(1 - v_p)} \frac{\partial c}{\partial x} \right) \quad (5)$$

where v_p is the volume fraction of the penetrant.

The film is symmetrical about its center axis for the purposes of diffusion, the $x = 0$ coordinate has been taken through the center of the film, with the faces across which diffusion takes place at $x = \pm l$. The boundary conditions are as follows: At the start of the desorption, the concentration of the penetrant throughout the film is the same and equal to the equilibrium concentration C^0 . The second boundary condition imposed is usually to require that concentration be zero at $x = l$ and $x = -l$ for all time, except at $t = 0$. Certain mathematical problems which arise as a result of this assumption will be dealt with in the discussion of results.

Free Volume Theory for the Dependence of the Diffusion Coefficient on Concentration

Fujita⁵ has extended the free volume theory of diffusion to account for the dependence of the diffusion coefficient on the concentration of the diffusing substance in polymers. The free volume is analogous to the "hole" which is opened up by thermal fluctuations of the polymer chains and is expressed as a fraction of the total volume of the system. The main points of the theory will be discussed, along with the final working equations.

The mobility of a species is assumed to be given by

$$m_a = A_a \exp(-B_a/f) \quad (6)$$

where m_a is the mobility of a species, B_a is an arbitrary parameter correspond-

ing to the minimum "hole" required for a diffusional displacement, A_d is a constant, and f is the fractional free volume. From the definition of the molar mobility, we have

$$D_T = RTm_d \quad (7)$$

where D_T is the thermodynamic diffusion coefficient. The free volume of the system is a function of the temperature and the concentration of the diffusing species and is assumed to be given by

$$f(v_p, T) = f(0, T) + \beta(T)v_p \quad (8)$$

where $f(v_p, T)$ is the fractional free volume of the system at temperature T and concentration v_p of the diffusing species, $f(0, T)$ is the fractional free volume of the polymer itself, and $\beta(T)$ is a proportionality constant relating the amount of free volume increase by the diffusing species. When $v_p = 1$, the free volume is that of the pure permeant, and for $v_p = 0$, the diffusion coefficient $D_{c=0}$ is given by

$$D_{c=0} = RTA_d \exp\{-B_d/f(0, T)\} \quad (9)$$

Combining eq. (6) with eq. (9) leads to the final expression for the thermodynamic diffusion coefficient:

$$\ln \frac{D_T}{D_{c=0}} = \frac{v_p}{[f(0, T)]^2/[B_d\beta(T)] + [F(0, T)/B_d]v_p} \quad (10)$$

The thermodynamic diffusion coefficient D_T can be related to D_{ab} by

$$D_T = \frac{D_{ab}}{(1 - v_p)} \frac{\partial \ln v_p}{\partial \ln a_p} \quad (11)$$

where a_p is the activity of the penetrant.

There are various theories which relate the volume fraction of the penetrant to the activity. The activity of the penetrant imbibed in amorphous polymers can be described in terms of the Flory-Huggins theory⁹:

$$\ln a_p = \ln v_p + (1 - v_p) + \chi(1 - v_p)^2 \quad (12a)$$

and

$$\frac{\partial \ln v_p}{\partial \ln a_p} = \frac{1}{(1 - v_p)(1 - 2\chi v_p)} \quad (12b)$$

where χ is the Flory-Huggins interaction parameter. Although χ is a function of temperature and concentration, for many systems it lies between 0.3 and 0.8. For instance, Barrer and Fergusson¹⁰ report values of χ ranging from 0.68 to 0.90 for benzene and polyethylene. Frensdorff¹¹ obtained values of χ of benzene and *n*-hexane in a polyethylene-polypropylene copolymer of 0.65 and 0.3, respectively. The computations carried out in the present work indicated that changes of 0.2 in the Flory-Huggins interaction parameter χ resulted in only a 10% change in the thermodynamic diffusion

coefficient. Therefore, a value of 0.5 was chosen for χ . The sensitivity of the computed free volume parameters to changes in χ are shown in the Appendix. Michaels and Hausslein¹² have used the Flory-Rehner equation to relate the activity of the penetrant to its volume fraction in crystalline polymers. An additional term was introduced to account for the enhanced activity of the penetrant resulting from contributions from the elastically deformed network (see Appendix). However, in the present work, it is assumed that this additional term can be neglected. Details showing the numerical implications of this simplifying assumption are given in the Appendix. Fujita⁵ shows that the "hole" parameter B_d can be interpreted as the ratio of the activation energy for diffusion at zero concentration to that of the activation energy of viscosity of the polymer itself. Williams *et al.*¹³ predict that the free volume of the polymer at its glass transition temperature is 0.025 and that it increases linearly with temperature at the rate of 4.8×10^{-4} per $^\circ\text{C}$.

Numerical Method for Solving the Diffusion Equation

The final form of the equation which is to be solved by numerical techniques is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[(1 - v_p)^2 \exp \left[\frac{v_p}{a + b v_p} \right] \cdot \frac{\partial c}{\partial x} \right] \quad (13)$$

where a is $[f(0,T)]^2/B_d\beta(T)$ and b is $f(0,T)/B_d$. Equation (13) can be written in dimensionless form by following the substitutions:

$$C' = c/C^\circ = v_p/V^\circ$$

where V° is the equilibrium volume fraction of the liquid in the polymer.

$$x' = x/l$$

$$t' = D_{c=0} t/l^2$$

Making these substitutions, and performing the differentiation, one obtains:

$$\frac{\partial C'}{\partial t'} = (1 - V^\circ C') \exp \left[\frac{C'}{A + BC'} \right] \left[\left\{ \frac{(1 - V^\circ C')A}{(A + BC')^2} - 2V^\circ \right\} \left[\frac{\partial C'}{\partial x'} \right]^2 + (1 - V^\circ C') \frac{\partial^2 C'}{\partial x'^2} \right] \quad (14)$$

where A is $[f(0,T)]^2/(B_d\beta(T)V^\circ)$ and B is $f(0,T)/B_d$. The partial differential equation, eq. (14), is then resolved into a series of 10 ordinary differential equations by dividing one-half of the membrane into 10 equal parts of width $\Delta x'$ and writing:

$$\frac{\partial C'}{\partial x'} = \frac{C'_{i+1} - C'_{i-1}}{2\Delta x'} \quad (15)$$

and

$$\frac{\partial^2 C'_i}{\partial x'^2} = \frac{C'_{i+1} - 2C'_i + C_{i-1}}{(\Delta x')^2} \quad (16)$$

Substitution into eq. (14) yields:

$$\begin{aligned} \frac{\partial C'_i}{\partial t'} = & (1 - V^0 C'_i) \exp \left[\frac{C'_i}{A + BC'_i} \right] \left[\left\{ \frac{(1 - V^0 C'_i)A}{(A + BC'_i)^2} - 2V^0 \right\} \right] \\ & \left\{ \frac{C'_{i+1}^2 - 2C'_{i+1} C'_{i+1} + C_{i-1}^2}{4(\Delta x')^2} \right\} + (1 - V^0 C'_i) \frac{(C'_{i+1} - 2C'_i + C'_{i-1})}{(\Delta x')^2} \end{aligned} \quad (17)$$

This equation is valid when $i = 2$ to 10. For the special case when $i = 1$, eq. (17) becomes

$$\frac{\partial C'_1}{\partial t'} = 2(1 - V^0 C'_1) \exp \left\{ \frac{C'_1}{A + BC'_1} \right\} \frac{C'_2 - C'_1}{(\Delta x')^2} \quad (18)$$

These ten differential equations are then solved using a 4th-order Runge-Kutta procedure as outlined in Ralston and Wilf.¹⁴ The results of the solution are, for given values of A and B , ten concentrations for values of time t' . The amount of liquid in the polymer at time t' is then calculated by numerical integration of the concentration profile. The integrated amounts $Q_i(t')$ can then be compared to the experimental values from desorption data and the parameters A and B can be changed so as to minimize the difference between the calculated and experimental amounts.

EXPERIMENTAL

Apparatus

The equipment used to measure desorption consisted of a Cahn Electrobalance, manufactured by Cahn Instrument Co., Paramount, California. The balance portion is an electromagnetic arrangement and beam pivoted at the center. At one end of the beam is a small metal flag which serves to intercept a light beam to a photocell circuit. If the beam is unbalanced by a slight amount, more or less light than the amount reaching the photocell at null point is sensed and an electric current flows in the electromagnet to rebalance the beam. The amount of current necessary to keep the beam balanced is directly proportional to the difference in weight at the two ends. This current is then converted to a 0-1 mV signal which is then recorded. The complete curve for weight versus time in the desorption process can thus be conveniently obtained.

The entire balance is placed in a glass bottle, 5 in. in diameter and 12 in. long. An aluminum plate through which the connecting wires are passed covers one end of the bottle. Two glass tapered-joint hangdown tubes are attached to the bottle, one surrounding the sample and the other surround-

ing the counterweights. A third tube is attached to the bottle so that the whole apparatus and sample may be placed under vacuum. The sample and counterweights are suspended on the balance by fine nichrome wires. The sample hangdown tube is surrounded by a circular Plexiglass tube through which water is circulated to keep the temperature constant. Vacuum is maintained by a Welch vacuum pump of 75 l./min capacity and the recorder used is a 1-mV full-scale Sargent three-speed model, having a 10-in. chart span.

The balance is calibrated with standardized weights and is theoretically sensitive to 10^{-7} g. In the experiments for this study, the amount desorbed was about 100 mg and the most sensitive range used was 1 mg full scale. Accuracy was limited by the mass dial on the instrument to about ± 0.1 mg.

Experimental Procedure

The samples used for the desorption studies were approximately 1.5 cm \times 6 cm and 10 mil (0.025 cm) thick. The weight of the sample was approximately 250 mg. A small hole was cut in the top of each sample for suspension on the balance. Prior to the desorption run, the polymer sample was immersed in the liquid to be desorbed until it had absorbed the equilibrium amount. This was accomplished by hanging the film in the liquid in a jacketed glass flask. Water maintained at the temperature of desorption was circulated through the jacket.

Before a run was started, the balance was first calibrated with the standardized weights. After sufficient time had been allowed for equilibrium absorption to take place, the sample was removed from the bath and hung on the balance. The sample hangdown tube was then fitted on the balance. The vacuum was turned on and the recorder was started. The time taken between the removal of the sample from the liquid and the start of recording the desorption was approximately 10 sec. The desorption was allowed to proceed until there was no significant weight decrease. This varied from 3 to 45 hr, depending on the system being studied.

Calculations

After each duplicate set of runs, the recorder chart data was digitized by taking about 200 points along the time axis and the corresponding ordinate. The values of $Q(t)$ for each of these points were then calculated. The equilibrium amount absorbed, $Q(0)$, was calculated from the difference between the initial and final weights of the sample. Then $\ln[Q(t)/Q(0)]$ was plotted against time for both runs. If there were significant discrepancies between the two runs, the run was repeated. It was found that discrepancies could arise from improper zero-time definition or from failure in removing the surface liquid from the sample before starting the desorption. The slope at long times was obtained by fitting a straight line subjectively to about the last ten points of the curve for computing $D_{c=0}$. McCall³ has shown that this slope is equal to $-D_{c=0} \pi^2/4l^2$.

To fit the solution of the differential equations, eqs. (17) and (18), the following procedure was used. A starting value of the parameters A and B was taken; $Q_I(t)$ was then calculated and the square of the difference between $Q_I(t)$ and $Q(t)$ was obtained and integrated over the time axis. This integrated error was then minimized by changing A and B . The search procedure to minimize the error consisted of fixing A and varying B until a 5% change in B produced a minimum error. The process was repeated with a new A . Reiteration of this scheme was continued until A and B were accurate to within 5%. These calculations were carried out on the IBM 360/75 computer at the Computing Center, University of Waterloo.

DISCUSSION

Numerical Solution of the Diffusion Equation

The numerical solution of the diffusion equation as outlined above posed some problems for the case of desorption of liquid from a film. These difficulties stemmed from the fact that the diffusion coefficient is an increasing function of the concentration of the diffusing species. Interestingly enough, similar difficulties do not arise when an absorption process is considered. If the diffusion coefficient, in general, is written

$$D_{ab} = D_{c=0}f(c), \quad (19)$$

then the diffusion equation in the x -direction becomes

$$\frac{\partial c}{\partial t} = D_{c=0} \left(\frac{\partial f(c)}{\partial c} \right) \left(\frac{\partial c}{\partial x} \right)^2 + D_{c=0} f(c) \left(\frac{\partial^2 c}{\partial x^2} \right). \quad (20)$$

In this equation, $[\partial f(c)]/\partial c$ and $(\partial c)^2/(\partial x)$ are always positive whether desorption or absorption is considered. However, in the case of desorption, $\partial^2 c/\partial x^2$ is negative, and $\partial c/\partial t$ is also negative. Thus for desorption, if the first term on the right-hand side is greater numerically than the second term, $\partial c/\partial t$ will be positive. This is physically incorrect for a desorption process. Since all of the terms are positive for absorption, the problem does not arise for this case. In other words, even though a given model of the diffusion coefficient does result in the solution of the diffusion equation for absorption, it may be impossible to solve the equation for the desorption case.

For the free volume model of the diffusion coefficient used in this study, the equations for the numerical solution appear as eqs. (17) and (18). In order to start the solution, the boundary conditions at the start and the concentration at the face of the membrane ($x' = 1$) must also be known. The first is straightforward and is

$$C'(0, x') = 1. \quad (21)$$

If, for the second boundary condition, one assumes that the concentration of the liquid is zero on the faces for all times greater than zero time, the nine

values of $\partial C'_i/\partial t'$ given by eqs. (17) and (18) will be zero at $t' = t' + \delta t'$; $\partial C'_{10}/\partial t'$ in this case will be given by

$$\frac{\partial C'_{10}}{\partial t'} = (1 - V^0) \exp \left\{ \frac{1}{A + B} \right\} \left\{ \frac{1}{4} \left[\frac{(1 - V^0)A}{(A + B)^2} - 2V^0 \right] - (1 - V^0) \right\} \quad (22)$$

Examination of eq. (22) shows that if

$$\frac{1}{4} \frac{(1 - V^1)A}{(A + B)^2} + 0.5 V^1 > 1,$$

$\partial C'_{10}/\partial t'$ becomes positive, resulting in an impossible physical situation. There is no physical reason why the inequality should not occur, and certainly the values of the parameters should not depend on whether the process is one of absorption or desorption.

In the present work, this difficulty was avoided by the use of a variable boundary condition in setting the value of the concentration at the surface of the film. Instead of this concentration being zero for all times except zero time, an exponential relation was assumed of the form

$$C'(1, t') = \exp(-kt') \quad (23)$$

where k is a constant for a given desorption run. In this form the liquid concentration at the surface would decrease relatively quickly from the initial equilibrium value to 0. The value of k was chosen by matching the rate of desorption with the rate that the vacuum pump could maintain at 10^{-3} mm Hg, about 50 l./min. The time t_0 for which 50 l./min was being desorbed was found and the product kt_0 was set equal to 15. Then k could be found and used in eq. (23) above. It required from 20 to 40 min for this condition to be achieved.

On examination of eq. (20), it is apparent that for absorption, the absolute value of $\partial c/\partial t$ will be larger than for desorption. The result of this is that a numerical solution will proceed much faster if absorption is being considered. Therefore, the numerical solution of the diffusion equation for the desorption case requires an extremely fast computer. In the present study, it required approximately 1 min of computing time on the IBM 360/75 to solve the equations for one value of the parameters A and B .

Another consideration which was found to be very important in the solution of the diffusion equation was the question of stability. Ames¹⁵ shows that the solution is stable if $D_{ab}\Delta t'/(\Delta x')^2$ is less than 0.5 for linear differential equations. In the present study, the value of $D_{ab}\Delta t'/(\Delta x')^2$ was set equal to 0.3, and it was found that no stability problems were encountered with this criterion. The accuracy of the solution was checked by comparing the solution with t' calculated from $D_{ab}\Delta t'/(\Delta x')^2 = 0.3$ and solutions with the stability criterion set at 0.15. Results shown in Table I indicate that the use of 0.3 for the stability criterion is sufficiently accurate.

TABLE I
Comparison of Concentration Profiles with Stability Criteria of 0.3 and 0.15

t'	$\frac{D\Delta t}{l^2}$	Values of x'										
		0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.010	0.3	0.7396	0.7374	0.7305	0.6188	0.7016	0.6781	0.6468	0.6052	0.5480	0.4629	0.2981
0.010	0.15	0.7399	0.7377	0.7308	0.7191	0.7019	0.6784	0.6472	0.6055	0.5484	0.4633	0.2981
0.031	0.3	0.4634	0.4616	0.4562	0.4468	0.4331	0.4143	0.3890	0.3549	0.3071	0.2324	0.0251
0.031	0.15	0.4635	0.4617	0.4563	0.4469	0.4332	0.4144	0.3891	0.3549	0.3071	0.2325	0.0251

Calculation of Free Volume Parameters

As mentioned before, the parameters A and B in eq. (14) were evaluated by minimizing the difference between the solution of the diffusion equation and the actual data obtained in the desorption runs. It was found that A and B could be estimated to within about 5%. In order to calculate the free volume parameters $f(0,T)$, $\beta(T)$, and B_d , one more equation is required. The one which was used was the expression for the free volume of the pure liquid,

$$f(1,T) = f(0,T) + \beta(T). \quad (24)$$

The difference in the free volume of the pure liquid at temperatures T_1 and T_2 is equal to the volumetric expansion of the liquid times the temperature difference.

The parameter B_d can thus be calculated between various temperatures. Theoretically, B_d is not a function of temperature. Although the results of the present work indicate variation with temperature, it is felt that the data are not accurate enough to assume that B_d is temperature dependent. As an approximation of B_d , the average of the values at the four temperatures was taken and assumed to remain constant. With these values of B_d , the free volume fraction at zero concentration $f(0,T)$ and $\beta(T)$ were calculated. An example of the free volume parameters and related diffusion data for benzene in polyethylene at 25°C is shown in Table II. Further numerical results and discussion of these parameters will be reported separately.

TABLE II
Free Volume Parameters for Benzene-Polyethylene System at 25°C

Parameter	Value	Units
A	0.106	
B	0.072	
$D_{c=0}$	1.25×10^{-8}	cm ² /sec
V^0	0.1483	
$f(0,T)$	0.0174	
$\beta(T)$	0.0795	
B_d	0.241	
	$\int_0^{t_N} (Q - Q_I)^2 dt$	0.5×10^{-5}

CONCLUSIONS

The method presented here of obtaining diffusion coefficient data for organic liquids in polymers yields sufficiently accurate values of the free volume parameters. The major disadvantage is the large amount of computer time required for solution of the diffusion equation. In subsequent papers^{16,17} it will be shown that a knowledge of the values of the free volume parameters enables one to make quantitative interpretations of the effect of

polymer modification and mixture composition on transport properties of organic liquid mixtures in polymer membranes.

APPENDIX

Examination of the Effect of Introducing Simplifying Assumptions in Evaluating the Term $(\partial \ln a_p)/(\partial \ln v_p)$

(a) In eq. (12), the term $(\partial \ln a_p)/(\partial \ln v_p)$ has been equated to $(1 - v_p)(1 - 2\chi v_p)$ and a value of 0.5 was set for χ . Strictly speaking, χ is not constant, but it will be shown below that this assumption does not lead to significant errors in the calculated numerical values of the free volume parameters A and B .

The effect of a change in $\partial \ln a_p/\partial \ln v_p$ can be compared to the effect of changes in A and B , by differentiation of

$$\frac{D_{ab}}{D_{c=0}} = \exp\left[\frac{v_p/V^0}{A + Bv_p/V^0}\right] (1 - v_p)F \quad (25)$$

where $F = \frac{\partial \ln a_p}{\partial \ln v_p}$.

$$\frac{\partial D_{ab}/D_{c=0}}{\partial F} = \exp\left[\frac{v_p/V^0}{A + Bv_p/V^0}\right] (1 - v_p) \quad (26)$$

$$\frac{\partial D_{ab}/D_{c=0}}{\partial A} = -\exp\left[\frac{v_p/V^0}{A + Bv_p/V^0}\right] (1 - v_p) \left[\frac{v_p/V^1}{(A + Bv_p/V^0)^2}\right] \quad (27)$$

$$\frac{\partial D_{ab}/D_{c=0}}{\partial B} = -\exp\left[\frac{V_p/V^0}{A + Bv_p/V^0}\right] (1 - v_p) \left[\frac{(v_p/v_0)^2}{(A + Bv_p/V^0)^2}\right] \quad (28)$$

For $(v_p/V^1) = 1$, it can be seen from the above 3 equations that

$$\frac{\partial F}{\partial A} = \frac{\partial F}{\partial B} = \frac{1}{(A + B)^2}$$

Typical values of A and B are about 0.1 and 0.08, respectively, therefore $\partial F/\partial A = 31$. Since A is accurate to about ± 0.005 , this would imply that F need be accurate to $\pm 0.005(31) = \pm 0.15$.

(b) Michaels and Hausslein¹² have used the Flory-Rehner equation to relate the activity of the permeant to its volume fraction in a crystalline polymer:

$$\ln a_p = \ln v_p + (1 - v_p) + \chi (1 - v_p)^2 + \frac{\langle \alpha \rangle_0^2 f \rho V_1}{M_c} (1 - v_p)^{1/3} \quad (29)$$

where V_1 is the molar volume of the permeant. The final term in eq. (29) was introduced to account for the enhanced activity of the penetrant resulting from the crystallinity.

The expression for $\frac{\partial \ln a_p}{\partial \ln v_p}$ now becomes

$$\frac{\partial \ln a_p}{\partial \ln v_p} = (1 - v_p) (1 - 2\chi v_p) - K \frac{v_p}{3(1 - v_p)^{2/3}} \quad (30)$$

where $K = \frac{\langle \alpha \rangle_0^2 f \rho V_1}{M_c}$.

To test the effect of an error in, and of leaving out the final term to account for the recrystallinity, eq. (30) can be differentiated with respect to χ and K as follows:

$$\frac{\partial F}{\partial \chi} = (1 - v_p) (-2v_p). \quad (31)$$

For $v_p = 0.15$, a typical value, $\partial F / \partial \chi = 0.255$.

Previously it has been shown that ∂F can be ± 0.15 . Thus $\partial \chi$ can be $\pm 0.15 / 0.255 = \pm 0.6$. The effect of omitting the term to account for the crystallinity can be seen similarly by differentiating F with respect to K :

$$\frac{\partial F}{\partial K} = \frac{V_p}{3(1 - v_p)^{2/3}}. \quad (32)$$

For $v_p = 0.15$, $\partial F / \partial K = 0.056$. Therefore, as ∂F can be ± 0.15 , ∂K can be $\pm 0.15 / 0.056 = \pm 2.7$. Referring to the results of Michaels and Hausslein, it is now possible to calculate an approximate value of K .

Values of up to about 0.90 are reported for the term $[\langle \alpha \rangle_0 f \rho V_1 / M_c] [(1 - v_p)^{1/3}]$. This value is for polyethylene having a weight fraction of 0.031 xylene. Using this data, it can be estimated that K would be about 0.66 and 0.98 for benzene and *b*-hexane, respectively. Since these values are considerably smaller than 2.7, it can be concluded that the omission of the term to account for the effect of the crystallinity on activity does not significantly affect the results of the present study.

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References

1. J. Crank, *The Mathematics of Diffusion*, Oxford University Press, Oxford, 1956
2. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, New York, 1968.
3. D. W. McCall, *J. Polym. Sci.*, **26**, 151 (1957).
4. M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).
5. H. Fujita, *Fortschr. Hochpolym.-Forsch.*, **3**, 1 (1961).
6. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 1960.
7. D. W. McCall and W. P. Slichter, *J. Amer. Chem. Soc.*, **80**, 1861 (1958).
8. H. A. Bent and J. Pinsky, Wright Air Development Center Report, Part 2, August 1955, pp. 53-133.

9. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N. Y., 1953.
10. R. M. Barrer and R. R. Ferguson, *Trans. Faraday Soc.*, **54**, 989 (1959).
11. H. K. Frensdorff, *J. Polym. Sci. A-2*, 333 (1964).
12. A. S. Michaels and Hausslein, *J. Polym. Sci. C*, **10**, 61 (1965).
13. M. L. Williams, R. F. Landel, and J. D. Fury, *J. Amer. Chem. Soc.*, **77**, 3701 (1955).
14. A. Ralston and H. S. Wilf, Eds., *Mathematical Methods for Digital Computers*, Wiley, New York, 1960.
15. W. F. Ames, *Non-Linear Partial Differential Equations in Engineering*, Academic Press, New York, 1965.
16. M. Fels and R. Y. M. Huang, *J. Macromol. Sci.*, to be published.
17. M. Fels and R. Y. M. Huang, *J. Appl. Polym. Sci.*, submitted for publication.

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