

Diffusivity and Solubility of Organic Vapors in Modified Polyethylene Films. I. Technique and Analysis of Results

OSMAN T. ABOUL-NASR* and ROBERT Y. M. HUANG, *Chemical Engineering Department, University of Waterloo, Waterloo, Ontario, Canada*

Synopsis

A new method of analyzing unsteady-state sorption data was developed to determine the diffusivity and solubility of vapors in polymer films. The equilibrium weight increase yields the solubility directly. Analysis of the unsteady-state data gives the diffusion coefficient and its concentration dependence. A complete method for the analysis of either absorption or desorption results is presented for any type of concentration dependence of the diffusion coefficient. In this paper the method is applied to the Fujita free volume theory. The apparatus and the experimental procedures are discussed in detail.

INTRODUCTION

Permeation of gases, vapors, and liquids through polymer membranes is an activated process. It occurs in three consecutive steps: dissolution, diffusion, and desorption.¹ Where there is a strong interaction between the permeant and the membrane, as in the case of most liquids and vapors, the diffusion coefficient, and hence the permeability, become concentration dependent. Since the solubility is a thermodynamic property while diffusion is a kinetic process, a study that allows for the independent determination of the solubility and the diffusivity would lead to a better understanding of the permeation process. Solubility and diffusivity data may be obtained from permeation experiments.

Frisch² proposed a method for the determination of these properties using a time lag technique. Dudas and Vrentas³ proposed a method of analyzing absorption runs without specifying a model for the concentration dependence of the diffusion coefficient. Fels and Huang⁴ proposed a desorption technique for the determination of the solubility and diffusion coefficients of vapors in polymer films. From a theoretical standpoint both absorption and desorption experiments furnish the same information necessary to determine the solubility and the diffusion coefficients. However, in desorption experiments one faces the problems of the exact and reproducible definition of the initial and boundary conditions required to solve the unsteady-state diffusion equation. Furthermore, the solubility results thus obtained are characteristic of the swollen film rather than the untreated one.

In this paper a new absorption technique is described. The steady-state results, or equilibrium results, yield the solubility of the vapor in the film directly,

* Present address: Department of Chemistry, University of Western Ontario, London, Ontario, Canada.

while analysis of the unsteady-state data leads to the determination of the diffusion coefficient and its concentration dependence.

THEORY

The Diffusion Equation

The general equation describing binary diffusion with no internal generation of mass and no bulk flow, is written in the form

$$\frac{\partial C_A}{\partial T} = \nabla^2 D_{AP} C_A \quad (1)$$

where C_A is the concentration of diffusant A (mole/length³), T is the time, D_{AP} is the diffusion coefficient of A with respect to membrane P (length²/time), and ∇ is the del operator, $\partial/\partial x + \partial/\partial y + \partial/\partial z$ (length⁻¹).

For thin films, where the thickness is small compared to the other dimensions, diffusion may be considered unidirectional; therefore,

$$\frac{\partial C_A}{\partial T} = \frac{\partial}{\partial X} \left(D_{AP} \frac{\partial C_A}{\partial X} \right) \quad (2)$$

In the case to be investigated, swelling of the film occurs on dissolution of the diffusant in the film. Therefore, the medium is no longer stationary with respect to any fixed set of axes. Equation (2) is modified to read⁴

$$\frac{\partial C_A}{\partial X} = \frac{\partial}{\partial X} \left(\frac{D_{AP}}{m_A} \frac{\partial m_A}{\partial X} \right) \quad (3)$$

where m_A is the mass fraction of the diffusant.

To solve this equation, a relation between the density and the composition must be known. For the systems under consideration, no theoretical relation is known. Additivity of the volumes is therefore assumed. This is not an inaccurate assumption. Solubility and swelling factors were reported by McCall and Slichter⁵ to be 12.6% by weight and 14% for *n*-hexane, respectively; and 17.2% by weight and 16% for benzene, both in polyethylene. Additive volumes would give swelling factors of 15% and 18% for *n*-hexane and benzene in polyethylene, respectively.⁴ Furthermore, Bent and Pinsky⁶ measured the experimental values of the swelling factor. These were found to be in the range of 15.2% to 17.2% for benzene-polyethylene at 70°F. Additive volume assumption gave a value of 16%.

Equation (3) is written as

$$\frac{\partial C_A}{\partial T} = \frac{\partial}{\partial X} \left(\frac{D_{AP}}{(1 - V_p)} \frac{\partial C_A}{\partial X} \right) \quad (4)$$

where V_p is the volume fraction of the polymer.

The solution of eq. (4) for constant D_{AP} was obtained analytically.⁷ Some cases of concentration-dependent diffusion coefficients were also solved analytically.⁸

Concentration Dependence of the Diffusion Coefficient

Applying Fujita's free volume theory,^{9,10} Fels and Huang arrived at the following expression for the concentration dependence of the diffusion coefficient⁴:

$$D_{AP} = D_{c=0} (1 - V_p)(1 - 2\chi V_p)^2 \exp\left(\frac{V_p}{A + BV_p}\right) \quad (5)$$

where χ is the Flory-Huggins interaction parameter; $A = [f(0, T)]^2/B_d\beta(T)$; $B = f(0, T)/B_d$; $f(0, T)$ is the fractional free volume of the polymer at temperature T ; B_d is an arbitrary constant corresponding to the minimum "hole" required for a diffusional jump; and $\beta(T)$ is a proportionality constant relating to the amount of free volume increase caused by the diffusing species at temperature T .

Citing literature data on χ , values between 0.3 and 0.8 were reported for the systems investigated in this study. It has also been reported that changes of 0.2 in χ would change D_T , the thermodynamic diffusion coefficient by less than 10%.⁴ It therefore seems both physically correct and mathematically convenient to use a value of 0.5 for χ .

Solution of the Diffusion Equation

Substituting the diffusion coefficient, as given by eq. (5), in eq. (4) we get

$$\begin{aligned} \frac{\partial C}{\partial T} = \frac{\partial}{\partial X} D_{c=0}(1 - V_p)^3 \exp\left(\frac{V_p}{A + BV_p}\right) \frac{\partial C}{\partial X} \\ = F_1(C) \left(\frac{\partial C}{\partial X}\right)^2 + F_2(C) \frac{\partial^2 C}{\partial X^2} \quad (6) \end{aligned}$$

where

$$\begin{aligned} F_1(C) = D_{c=0}(1 - \alpha C)^3 \exp\left(\frac{C}{(A/\alpha) + BC}\right) \left[\frac{A/\alpha}{[(A/\alpha) + BC]^2} - \frac{3}{1 - \alpha C} \right] \\ F_2(C) = D_{c=0}(1 - \alpha C)^3 \exp\left(\frac{C}{(A/\alpha) + BC}\right) \end{aligned}$$

and α is a conversion factor from volume fraction to weight fraction.

Because of the little difference in density between the diffusant and the polymer, α may be taken to be equal to unity. Equation (6) holds for any Fickian diffusion process where the diffusion coefficient is concentration dependent; $F_2(C)$ describes this dependence; and $F_1(C) = \partial(F_2(C))/\partial C$. Given the present dependence of the diffusion coefficient on the concentration, eq. (6) becomes a second-order, second-degree partial differential equation with variable coefficients. No analytical solutions are available for this case or similar cases. A numerical method was therefore employed.

Dividing the film into two symmetrical halves, the initial and boundary conditions may be written as

Initial condition

$$C = 0, \quad 0 < |X| < L, \quad T \leq 0 \quad (7a)$$

Boundary condition 1

$$C = C^0, \quad X = \pm L, \quad T \geq 0 \quad (7b)$$

Boundary condition 2

$$\frac{\partial C}{\partial X} = 0, \quad X = 0, \quad T \geq 0 \quad (7c)$$

where C^0 is the saturation concentration of the diffusant (weight/weight) and $2L$ is the thickness of the film.

The choice of the boundary condition (7b) is backed by theoretical and experimental evidence: the choice of the value for the χ parameter indicates a fair amount of interaction. If the diffusion coefficient is only concentration dependent, which is the case studied here, it is not unreasonable to assume that molecular rearrangement in the surface layer proceeds at a very high rate.¹³ Richman and Long,¹⁴ using a microradiographic technique, found that the conditions of constant surface concentration is held from the very beginning of the experiment for the system methyl alcohol-poly(vinyl acetate) at 30°C.

Using the following substitutions

$$c = \frac{C}{C^0} \quad (8a)$$

$$x = \frac{X}{L} \quad (8b)$$

$$t = \frac{(D_{c=0}T)}{L^2} \quad (8c)$$

Equation (6) is rewritten in the following dimensionless form:

$$c_t = f_1(c)c_x^2 + f_2(c)c_{xx} \quad (9)$$

where

$$f_2(c) = (1 - c)^3 \exp \left[\frac{c}{a + bc} \right]$$

$$f_1(c) = f_2(c) \left[\frac{a}{(a + bc)^2} - \frac{3}{1 - c} \right]$$

$$a = \frac{[f(0, T)]^2}{B_d \beta(T) V^0}$$

$$b = \frac{f(0, T)}{B_d}$$

$$c_x = \frac{\partial c}{\partial x}, \quad c_{xx} = \frac{\partial^2 c}{\partial x^2}, \quad c_t = \frac{\partial c}{\partial t}$$

and V^0 is the saturation volume concentration.

The initial and boundary conditions become

Initial condition

$$c = 1, \quad t \geq 0, \quad x = 0 \quad (10a)$$

Boundary condition 1

$$c_x = 0, \quad t \geq 0, \quad x = 1 \quad (10b)$$

Boundary condition 2

$$c = 0, \quad t \leq 0, \quad 0 < x \leq 1 \quad (10c)$$

Using the net equations suggested by Liu^{15,16}

$$c_t(j,i) = \frac{1}{\Delta t} [c(j+1,i) - c(j,i)] \quad (11a)$$

$$\begin{aligned} c_x(j,i) &= \frac{1}{2} [c_x(j+1,i) + c_x(j+1)] \\ &= \frac{1}{4\Delta x} [c(j+1,i-2) - 4c(j+1,i-1) + 3c(j+1,i) \\ &\quad + c(j,i+1) - c(j,i-1)] \quad (11b) \end{aligned}$$

$$\begin{aligned} c_{xx}(j,i) &= \frac{1}{\Delta x} [c_x(j,i+1) - c_x(j+1,i)] \\ &= \frac{1}{2(\Delta x)^2} [c(j,i-1) - 4c(j,i) + 3c(j,i+1) \\ &\quad - c(j+1,i-2) + 4c(j+1,i-1) - 3c(j+1,i)] \quad (11c) \end{aligned}$$

The j 's refer to the position in the time space and the i 's refer to the distance space.

Substituting from eq. (11) into eq. (6) and solving for $c(j+1,i)$ we get

$$c(j+1,i) = \frac{G_1 + 4(G_2 + G_3)}{3} \quad (12)$$

where

$$G_1 = 4c(j+1,i-1) + c(j,i-1) - c(j+1,i-2) - c(j,i+1)$$

$$G_2 = \frac{f_2(c)}{f_1(c)} + \frac{2}{\epsilon f_1(c)}$$

$$G_3 = \left[G_2^2 + \left\{ \frac{G_1 - 3c(j,i)}{\epsilon f_1(c)} \right\} + \frac{2f_2(c)}{f_1(c)} \{c(j,i) - c(j,i-1)\} \right]^{1/2}$$

and $\epsilon = (\Delta x)^2/\Delta t$.

The functions $f_1(c)$ and $f_2(c)$ are to be determined at $c(j,i)$. Using this formula for $i = 1$, an expression containing $c(j+1, -1)$, that is, a point lying behind the surface ($x = 0$ or $i = 0$) is obtained. To overcome this hypothetical node, we apply Saul'yev's four-point formula¹⁷ at $i = 0$. Since the concentration at the surface is time independent, we need to use only the expressions for c_x and c_{xx} :

$$c_x(j,0) = \frac{1}{\Delta x} [c(j,1) - c(j,0)] \quad (13a)$$

$$\begin{aligned} c_{xx}(j,0) &= \frac{1}{\Delta x^2} [c(j+1, -1) - c(j+1,0) - c(j,0) + c(j,1)] \\ &= \frac{1}{\Delta x^2} [c(j+1, -1) + c(j,1) - 2c(j,0)] \quad (13b) \end{aligned}$$

Solving eq. (13) simultaneously with the form of eq. (11) containing $c(j+1, -1)$, we obtain the following expression for $c(j+1,1)$:

$$c(j+1,1) = [H_1 + 4(H_2 + H_3)]/3 \quad (14)$$

where

$$H_1 = \frac{f_2^{(1)}(c)}{f_1^{(1)}(c)} + 3c(j-1,1) - c(j,2) + c(j,3)$$

$$H_2 = \frac{f_2^{(2)}(c)}{f_1^{(2)}(c)} + \frac{2}{f_1^{(2)}(c)}$$

and

$$H_3 = \left[H_2^2 + \frac{H_1}{3f_1^{(2)}(c)} + \left\{ \frac{2f_2^{(2)}(c)}{f_1^{(2)}(c)} [c(j,2) - c(j,3)] \right\} \right]^{1/2}$$

The superscripts refer to the position in the distance space at which $f_1(c)$ and $f_2(c)$ should be evaluated. For the points $(j+1, i)$ at $x = 1$, terms containing $c(j, i+1)$, behind the boundary, appear in the expressions. This may be avoided by using the symmetry condition (10b) and substituting $c(j, i-1)$ for $c(j, i+1)$.

Evaluation of the Parameters

This was done using a simplex technique proposed by Nelder and Meade.¹⁸ Four initial guesses, each constituted of a set of values of $D_{c=0}$, a and b , were supplied to the program. Solution of eq. (6) was performed using each set separately. This would give four concentration distributions. The solution was interrupted at various time levels and the profiles were integrated numerically with respect to x giving values of the total amount of diffusant present in the film at the particular time level. These amounts were compared to the observed experimental value with the objective of minimizing the absolute value of the difference. This procedure would give progressively better sets of parameters. The next stage in solving eq. (6) was started using the four sets obtained at the conclusion of the previous stage. This step was repeated until the steady state was reached. All the best values obtained at various time levels were averaged to give the values of the parameters for the run. $D_{c=0}$ was obtained directly while $f(0, T)$, $\beta(T)$, and B_d were obtained by solving the following three equations:

$$a = \frac{[f(0, T)]^2}{B_d \beta(T) V^0} \quad (15)$$

$$b = \frac{f(0, T)}{B_d} \quad (16)$$

$$f(1, T_1) = f(1, T_2) + \alpha_A (T_1 - T_2) \quad (17)$$

where α_A is the thermal expansion coefficient of the diffusant. Equation (17) represents the free volume of the diffusant. Implicit in this set of equations is the valid assumption of the additivity of free volumes.¹⁸ The assumption that B_d is equal to unity⁴ is also avoided.

EXPERIMENTAL

Apparatus

The experimental setup consisted of three main parts: the vapor source, the electrobalance, and the vacuum system. A schematic diagram of the setup is shown in Figure 1.

The Vapor Source. This consisted of a separating funnel A connected to a three-necked bottle B along a 12-mm vacuum glass tubing fitted with two vacuum stop-cocks V1 and V2. The funnel was used to introduce the solvent used, or the condensate, collected in a later stage, to bottle B. Bottle B was placed in a temperature-controlled water bath. Temperature was regulated to within $\pm 0.1^\circ\text{C}$ of the desired value. The first neck of B was connected to the funnel A. The second was connected to the balance by a 6-mm vacuum glass tubing fitted with stopcock V3. The third neck was connected to the vacuum pump by a 6-mm vacuum rubber tubing. A stopcock, V4, regulated this line.

The Electrobalance. A detailed description of the mechanisms of operation of the balance is given elsewhere.⁴ The entire balance was placed in a 12.5-cm-diameter, 30-cm-long glass tube. Three glass-joint hangdown tubes were attached to it. One surrounded the weight pan. The second led to the vacuum system. The third was jacketed with a Plexiglas tube. Water was circulated inside the jacket at temperatures within $\pm 0.1^\circ\text{C}$ of the required values. The sample and the counterweights were suspended at the ends of the beam by means of similar fine nichrome wire. A weight-time curve was obtained. The balance was calibrated with standard weights. Accuracy of measurement was ± 0.001 mg (usually less than 0.1%).

The Vacuum System. A vacuum gauge G was connected to the system next to the vapor exit from the balance. Two cold traps, K1 and K2, were used alternatively to collect the vapors. Dry ice-acetone mixtures were used to condense the vapors. Vacuum was maintained in the system by a Sargent vacuum pump of 35 l./min capacity.

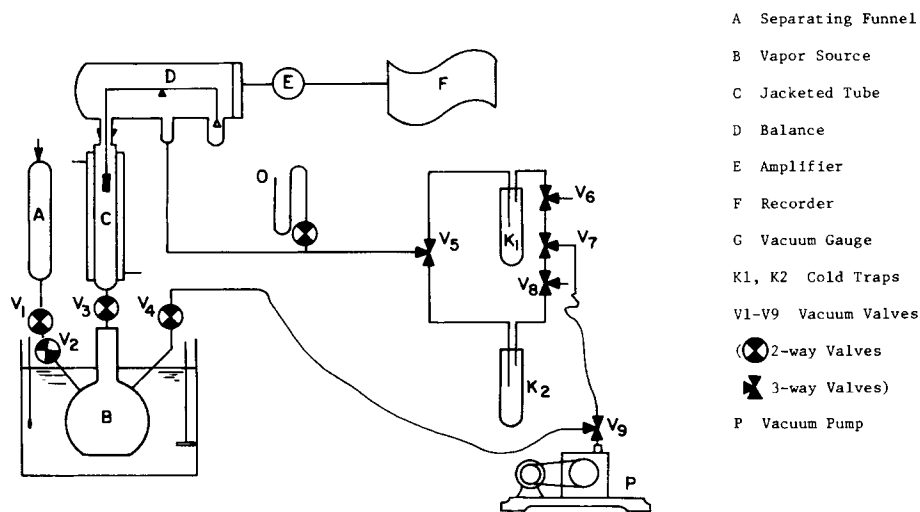


Fig. 1. Schematic diagram of the apparatus.

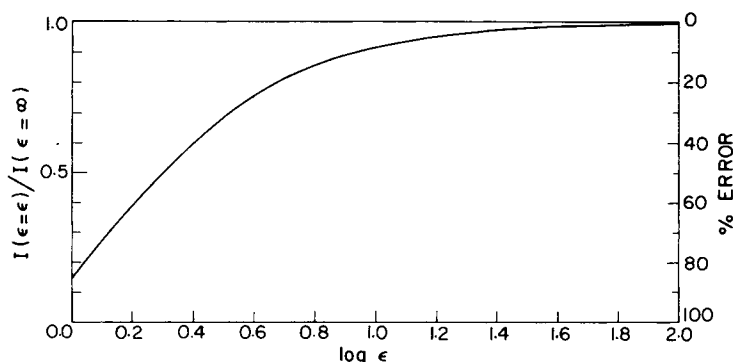


Fig. 3. Effect of mesh size on the solution.

expansion of vapors, already present in the vapor source, when V3 was to be opened. Such an expansion would lead to the following: first, the temperature of the vapor would decrease because of this throttling and it would condense on the film, leading to substantial errors both in the early and the later stages of the experiment. Second, large currents of vapor would flow through the weighing compartment, disturbing the position of the sample and giving erratic readings. Furthermore, since the vapor space in the vapor source could not have been immersed completely under water, these vapors might have been at a slightly different temperature.

(4) After pressure and temperature equilibria were attained, V3 was opened and V4 was closed. Simultaneously, weight recording was started.

(5) The vapors were directed to either cold trap K1 or K2 by proper manipulation of valves V5, V6, V7, and V8. Whenever an appreciable amount of

TABLE I
Effect of Mesh Size ϵ on Concentration Profile^a

β	$\epsilon = 20$	$\epsilon = 30$	$\epsilon = 100$
Node no.	C	C	C
1	1.0000	1.0000	1.0000
2	1.0000	1.0000	1.0000
3	0.8532	0.8581	0.8656
4	0.6623	0.6733	0.6886
5	0.4633	0.4847	0.5011
6	0.2717	0.2911	0.3167
7	0.1049	0.1073	0.1486
8	0.0136	0.0202	0.0314
9	0.0000	0.0000	0.0000
10	0.0000	0.0000	0.0000
11	0.0000	0.0000	0.0000
12	0.0000	0.0000	0.0000
13	0.0000	0.0000	0.0000
14	0.0000	0.0000	0.0000
15	0.0000	0.0000	0.0000
16	0.0000	0.0000	0.0000
Integral	2.1612	2.2048	2.2635
% Error	4.75	2.01	0.50

^a $a = 0.095$; $b = 0.075$; $D_{c=0} = 0.2 \times 10^{-8}$.

condensate was collected in one trap, vapor flow was diverted to the other. The condensate was then reintroduced in the system through A. This was done very slowly to avoid any pressure disturbances within the system.

(6) The steady-state weight increase was determined to within ± 0.005 – 0.01 mg, less than 0.1%–0.2% of the total weight increase. The time required to reach the steady state was determined to within ± 15 sec, an error of 0.2%–1.2% according to the total time of the run.

(7) To reduce the buildup of static charges on the jacketed hangdown tube and to avoid their subsequent effects on the weight, a small amount of NaCl was added to the circulating water to ground the jacket.

RESULTS AND DISCUSSION

Inspection of eq. (6) shows that it is absolutely unstable for $C_x > 0$, marginally stable for $C_x = 0$, and absolutely stable for $C_x < 0$. To satisfy stability requirements, only the right-hand scheme suggested by Liu,^{15,16} rather than the averaging or alternating methods, was used. A computer program for the numerical solution and evaluation of the parameters was written. A simplified flow chart of this program is shown in Figure 2.

Owing to the use of a numerical scheme, integration was not carried out at exactly 0.2 of the total time. This necessitated the weight averaging of the resulting parameters regarding the time before the integration and the difference between the value of this integral and the experimental value. The final average values were checked by following the progress of the concentration profile and its integral and checking them at intermediate stages other than those at which the optimization was carried out.

The Mesh Size

From the boundary conditions, eq. (7), as well as from the nature of the system and eq. (6), it is evident that a fine mesh must be used to assure both stability and convergence. The necessary and sufficient conditions for stability are more

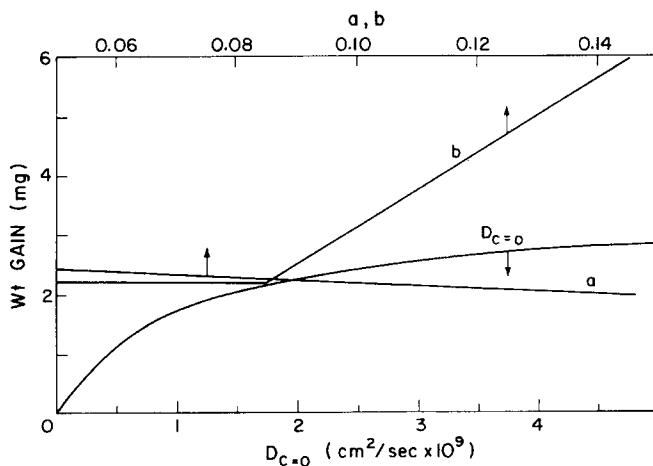


Fig. 4. Effect of a , b , and $D_{c=0}$ on the value of the integral.

stringent than the necessary and sufficient conditions for convergence.¹⁷ Provided that the approximation and truncation errors are small throughout the x and t domains, stability implies convergence. These errors were minimized through the use of double-precision numbers (16 significant figures).

It is claimed that this mesh equation is stable for all positive values of ϵ ($= \Delta x^2 / \Delta t$).¹⁵ Although finer mesh size guarantees convergence and stability, it requires longer computation times. The optimum value of ϵ was taken as the value larger than the change in the values of both the integral, and the concentrations at the individual space nodes were minor. Various values of ϵ (between 0.1 and 100) were tried and then plotted against the value of the integral (I) in Figure 3. The integral is very sensitive to changes in ϵ at low values of ϵ . At values of ϵ larger than 20, the change becomes less than 1% of the value at $\epsilon = 100$. A value of ϵ equal to 30 was taken throughout this work. Table I shows the effect of ϵ on the value of the integral and the individual concentration after 20% of the time for $\epsilon = 20, 30$, and 100. The use of finer mesh size, $\epsilon = 100$, in the range $x < 0.1$ and $t < 0.1$ required longer computer times without improving the results significantly. It was therefore concluded that a fixed step size was sufficiently accurate.

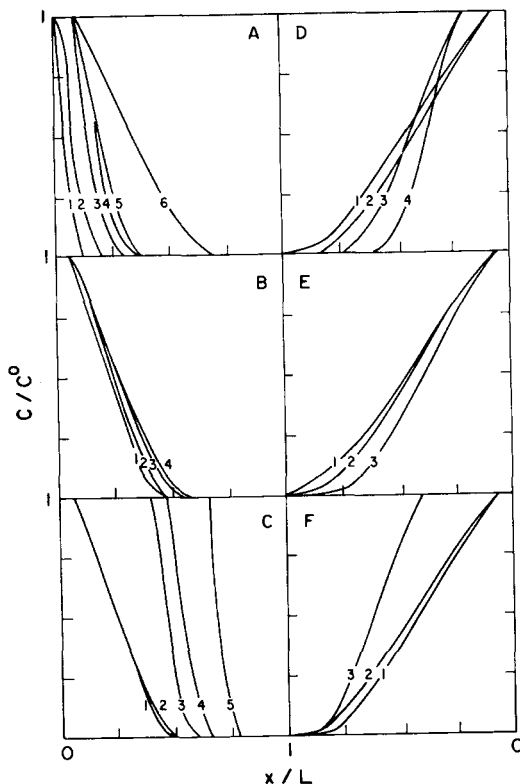


Fig. 5. Effect of variation of a , b , and $D_{c=0}$ on concentration profile at $t = 0.2$. A: $a = 0.1$; $b = 0.06$; $D_{c=0} = 0.1$ (1), 0.35 (2), 0.6 (3), 0.85 (4), 1.1 (5), and 4.5 (6). B: $D_{c=0} = 0.2$; $b = 0.2$; $a = 0.145$ (1), 0.1 (2), 0.07 (3), and 0.05 (4). C: $a = 0.095$; $D_{c=0} = 0.2$; $b = 0.065$ (1), 0.09 (2), 0.11 (3), 0.125 (4), and 0.145 (5). D: $a = 0.07$, $b = 0.075$, $D_{c=0} = 0.6$ (1); $a = 0.09$, $b = 0.085$, $D_{c=0} = 0.71$ (2); $a = 0.099$, $b = 0.089$, $D_{c=0} = 0.35$ (3); and $a = 0.12$, $b = 0.09$, $D_{c=0} = 0.23$ (4). E: $a = 0.064$, $b = 0.069$, $D_{c=0} = 0.5$ (1); $a = 0.075$, $b = 0.085$, $D_{c=0} = 0.45$ (2); $a = 0.102$, $b = 0.087$, $D_{c=0} = 0.5$ (3). F: $a = 0.09$, $b = 0.08$, $D_{c=0} = 0.4$ (1); $a = 0.075$, $b = 0.078$, $D_{c=0} = 0.8$ (2); $a = 0.09$, $b = 0.078$, $D_{c=0} = 0.8$ (3). All $D_{c=0}$ values are to be multiplied by 10^{-8} .

Effect of the Free Volume Parameters

It is very difficult to determine analytically the sensitivity of the solution, i.e., the concentration profile, to the variations in the free volume parameters $D_{c=0}$, a , and b , eq. (9). This was studied numerically by changing the values of each of these parameters, one at a time, over the whole range of its expected variation. This is shown in Figure 4. As shown, the value of the integral is more sensitive to variations in $D_{c=0}$ than it is to variations in either a or b . (The second part of the broken line describing the dependence of I on b was found to yield physically unrealistic results.) This resulted in problems in the determination of the exact optimum values of a and b . This problem was overcome to a large extent in the following way. Using the simplex technique discussed earlier, the solution was allowed to converge to within $\pm 5\%$ of the observed value through the simultaneous change of the three parameters. At this stage, the program was stopped. It was started again through the variation of a and b only until it converged to within $\pm 1\%$. Finer convergence was obtained by varying the three parameters simultaneously once more. This technique improved the results over the values obtained by the one-stage method.

The simultaneous variation of $D_{c=0}$, a , and b show some interesting results. In fact, a and b are interrelated, see eqs. (15) and (16). For low values of b and high values of a , indicating low concentration dependence, the concentration profile is a uniformly decreasing one showing a deeper penetration. The depth of the penetration increases with increasing $D_{c=0}$. It approaches the case of concentration-independent diffusion coefficient for very high values of a and very low values of b . On the other hand, high values of b and low values of a , indicating high concentration dependence, lead to plug-like concentration profile, the concentration being high near the surface and dropping sharply toward the center. Concentration profiles for different combinations of $D_{c=0}$, a , and b are shown in Figure 5.

Figure 6 shows a typical absorption curve for heptane in polyethylene modified by annealing a heptane after being subjected to gamma-ray irradiation for 25 hr at a dose rate of 0.602 Mrad/hr. The points shown on the graph are those

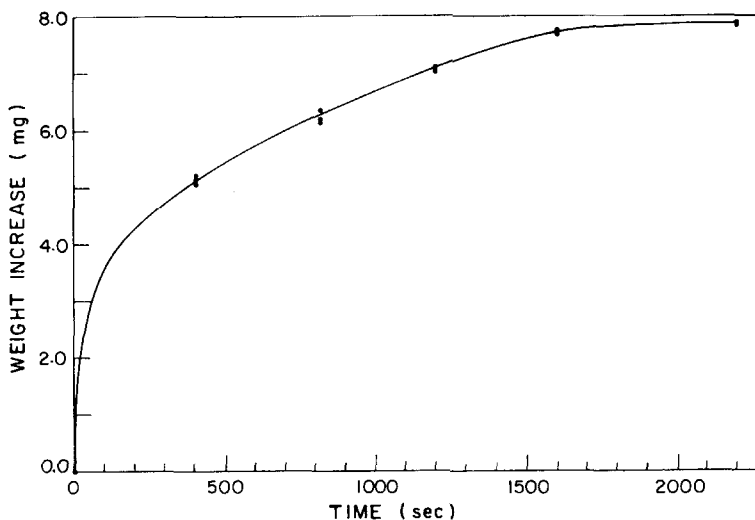


Fig. 6. Comparison between the proposed analytical solution and the observed absorption behaviour.

obtained from the best fit at various stages, while the solid line represents the experimental data. The agreement between the two results is typical of more than 200 runs described elsewhere.¹⁹

An improvement over the aforementioned technique may be as follows: a desorption run is to be started right after the equilibrium absorption has been reached. From the final stages of the desorption run, when the concentration is very small, an approximate value of $D_{c=0}$ may be calculated. Evaluation of a and b may follow the aforementioned three-stage technique after deleting the first stage.

CONCLUSIONS

A new experimental method for the separate and simultaneous analysis of the solubility and diffusivity of vapors in polymer films has been presented. The absorption technique mentioned is superior to desorption techniques in many ways. First, the properties measured are more indicative of the untreated network rather than of the swollen one. Second, the boundary conditions proposed are both nearer to the actual physical situation and more amenable to mathematical treatment. Furthermore, the assumptions made are minimal and realistic. The method of analysis of data may be adopted for both absorption and desorption experiments as well as for any form of concentration dependence of diffusivity. Experimental results on the diffusivity¹⁹ and the solubility²⁰ of various organic vapors in modified polyethylene films will be reported later.

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