Mathematical Analysis of Sorption Experiments

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A new technique is derived for determining the concentration dependence of diffusion coefficients from sorption experiments. In this analysis the diffusion equation including the effects of phase volume change and volume change on mixing is solved by a weighted residual method to produce approximate analytical expressions which describe the sorption process. It is possible to deduce the concentration dependence of the diffusion coefficient from a single sorption experiment without assuming the form of the diffusivity-concentration relationship. A direct evaluation of the technique is obtained from the analysis of test data generated by finite-difference solutions of the equations which portray the sorption process.

The measurement of diffusivities of relatively low molecular weight materials in polymers and polymer melts is necessary for the analysis of many polymer processing steps. The sorption and permeation methods are the two most commonly used techniques for determining the diffusion coefficients for polymer-penetrant systems. In a permeation experiment, the amount of penetrant diffusing through a film of polymer is measured as a function of time under the conditions that the two surfaces of the film are exposed to two different penetrant vapor pressures. In a sorption experiment, the amount of penetrant absorbed or desorbed by a film of solid polymer or a pool of molten polymer is measured as a function of time. In the conventional sorption experiment a polymer sample which is in equilibrium with a specific penetrant vapor pressure is suddenly exposed to a different vapor pressure level and the approach to the new equilibrium state is followed by direct weighing of the polymer sample. The data from such an experiment are usually represented by a sorption curve which is a plot of the fractional approach to the final equilibrium state as a function of the square root of time. As pointed out by Crank and Park (*1*), the sorption method has several advantages over the permeation method and several experimental techniques have been developed for accurately measuring the polymer weight as a function of time.

The major problem associated with the sorption technique is the fact that it is difficult with the available methods of data analysis to determine the concentration dependence of the diffusivity. This is a significant disadvantage since the diffusion coefficients of many penetrants which are of industrial importance, such as monomers, plasticizers, and blowing agents, exhibit a very strong dependence on the concentration level. A variety of methods has been proposed for the determination of the concentration dependence of the diffusion coefficient from sorption measurements (*2* to *8*). In all of these methods a series of sorption experiments at different concentration levels is required to determine the concentration dependence. Essentially only one piece of information is extracted from each sorption curve, so that many experiments may be required to achieve good accuracy. This is especially true for the methods which require graphical or numerical differentiation of the results deduced from each experimental curve. Some of the above methods are further restricted to a specific functional dependence of the diffusion coefficient on the concentration, and several are limited to the use of data obtained during the initial stages of the experiment where the sorption process can be approximated by considering diffusion in a semi-infinite medium. Finally, a few of the methods are applicable only to reverting sorption experiments (*3*) which are more time-consuming than progressing sorption experiments.

It is well known (*9*, *10*) that a qualitative estimate of the concentration dependence of the diffusivity can be readily ascertained from an inspection of the shape of a single sorption curve. However, a method of analyzing one sorption curve to determine quantitatively the concentration dependence of the diffusivity has not been developed. The absence of such a method is no doubt due to the fact that information concerning the value of the diffusivity at some specific concentration is masked in the sorption data which represent the integrals of the concentrations throughout the complete polymer sample at specific instances in time. With data from one sorption curve the available techniques are limited to determining a diffusivity which is some average over the complete concentration range or to establishing the diffusivity at only the final equilibrium concentration (*11*). What is needed for a detailed analysis of a single sorption curve is a solution of the diffusion equation for an arbitrary diffusivity-concentration relationship.

Generally, there are two basic problems of interest when investigating concentration-dependent diffusion phenomena. The direct problem consists of determining concentration profiles and quantities of matter transferred for a given diffusion coefficient-concentration functional relationship and a given geometry. The inverse problem involves determining from experimental concentration profiles, sorption curves, or other types of data the diffusivity-concentration relationship. The direct problem obviously involves the solution of the diffusion equation and so does the inverse problem, except for special cases such as the analysis of free diffusion experiments. In addition, it is often true that resolving the inverse problem is simpler than dealing with the direct problem. It will be seen later that such is the case for the analysis of sorption data.

The absence of analytical solutions to the nonlinear diffusion equation which describes mass transfer with a concentration-dependent diffusivity in a sheet precludes the possibility of obtaining an exact result for the diffusivity-concentration functional relationship from one experimental curve. However, in this paper we obtain an approximate analytical solution to the inverse problem using a weighted residual method. This method of determining the diffusion coefficient as a function of concentration from one sorption curve requires no prior knowledge of the functional form of the concentration dependence. In addition, the effect of the change of the polymer sample thickness due to phase volume change and the effect of volume change on mixing are also incorporated into this development. In the last section of the paper, the accuracy and limitations of this new technique are determined by analyzing sorption data generated by finite-difference solutions of the partial differential equation describing the sorption process.

FORMULATION OF PROBLEM

Consider a typical sorption experiment where a sample of solid or molten polymer is subjected to a step change in pressure of an essentially pure fluid phase of the penetrant. The experiment is carried out isothermally, and it is assumed that the penetrant reaches its equilibrium concentration at the surface instantaneously and maintains it during the course of the experiment. It is further assumed that the penetrant does not react with the polymer and that the geometry of the polymer sample is such that diffusion and phase change are effectively one-directional phenomena. In addition, the analysis is restricted to experiments conducted under conditions where relaxation and rearrangement of polymer molecules are very fast compared to the rate of diffusion, so that a linear constitutive equation for the diffusion flux and a diffusion coefficient depending only on concentration suffice to describe the transport process in the polymer. Finally, we presume that the total density of the binary polymer-rich phase is affected negligibly by the pressure variation which itself should be very small for any diffusion-generated flow. The mass transport process in the polymer, and hence the sorption experiment, can be described by a relatively complex set of equations when written in terms of usual concentration and length variables. These equations, which are presented elsewhere (*12*), are simply the result of combining the species and total continuity equations with a thermal equation of state and appropriate jump and boundary conditions.

Rather than work with this set of equations in describing the general sorption problem, we convert the equations of change to a simpler form by utilizing different length and concentration variables following a suggestion by Crank (*10*). The species continuity equations for the penetrant and polymer can be written as

$$\frac{\partial \rho_I}{\partial t} + \frac{\partial(\rho_I v_I)}{\partial x} = 0 \tag{1}$$

$$\frac{\partial \rho_J}{\partial t} + \frac{\partial(\rho_J v_J)}{\partial x} = 0 \tag{2}$$

and the thermal equation of state takes the form

$$\rho = \rho(\rho_I) \tag{3}$$

We can also write

$$\rho_I v_I = \rho_I v_J + j_I^0 \tag{4}$$

Hence, utilization of a new concentration variable

$$q_I = \frac{\rho_I}{\rho_J \hat{V}_J^0} \tag{5}$$

and a new length variable

$$\xi(x, t) = \int_0^x \hat{V}_J^0 \rho_J(x', t)\, dx' \tag{6}$$

in conjunction with Equations (2) and (4) yields the following result for Equation (1):

$$\left(\frac{\partial q_I}{\partial t}\right)_\xi = -\left(\frac{\partial j_I^0}{\partial \xi}\right)_t \tag{7}$$

The proper constitutive equation for the mass diffusion flux relative to the mass average velocity is (*13*)

$$j_I = -\rho D \frac{\partial \omega_I}{\partial x} \tag{8}$$

and it can easily be shown that

$$j_I^0 = \frac{j_I}{\omega_J} = -\frac{\rho D}{\omega_J} \frac{\partial \omega_I}{\partial x} \tag{9}$$

or, in terms of the new concentration and distance variables

$$j_I^0 = -D\rho_J^2 (\hat{V}_J^0)^2 \left(\frac{\partial q_I}{\partial \xi}\right)_t \tag{10}$$

Substitution of Equation (10) into Equation (7) gives

$$\left(\frac{\partial q_I}{\partial t}\right)_\xi = \frac{\partial}{\partial \xi}\left[F(q_I) \frac{\partial q_I}{\partial \xi}\right] \tag{11}$$

where

$$F(q_I) = D\rho_J^2 (\hat{V}_J^0)^2 \tag{12}$$

Equation (11) is a nonlinear parabolic partial differential equation describing the sorption process in the polymer sheet subject to the following boundary conditions:

$$\left(\frac{\partial q_I}{\partial \xi}\right)_{\xi=0} = 0 \tag{13}$$

$$q_I(\xi_L, t) = q_{IE} \tag{14}$$

$$q_I(\xi, 0) = q_{IO} \tag{15}$$

$$\xi_L = \hat{V}_J^0 \rho_{JO} L \tag{16}$$

$$X(0) = L \tag{17}$$

It can also be easily shown that

$$M_I = \int_0^{\xi_L} (q_I - q_{IO})\, d\xi \tag{18}$$

$$X(\infty) = \frac{\rho_{JO} L}{\rho_{JE}} \tag{19}$$

$$M_{I\infty} = \xi_L (q_{IE} - q_{IO}) \tag{20}$$

It is evident that the change of variables has eliminated the moving boundary problem by concentrating this nonlinearity in the partial differential equation itself.

Finally, utilization of the dimensionless variables

$$q_I^* = \frac{q_I - q_{IO}}{q_{IE} - q_{IO}} \tag{21}$$

$$\xi^* = \frac{\xi}{\xi_L} \tag{22}$$

$$t^* = \frac{tD_0}{\xi_L^2} \tag{23}$$

in Equations (11), (13) to (15), (18), and (20) gives

$$\frac{\partial q_I}{\partial t} = \frac{\partial}{\partial \xi}\left[\frac{F(q_I)}{D_0} \frac{\partial q_I}{\partial \xi}\right] \tag{24}$$

$$\left(\frac{\partial q_I}{\partial \xi}\right)_{\xi=0} = 0 \tag{25}$$

$$q_I(1, t) = 1 \tag{26}$$

$$q_I(\xi, 0) = 0 \tag{27}$$

$$\frac{M_I}{M_{I\infty}} = \int_0^1 q_I\, d\xi \tag{28}$$

where the asterisks have been dropped for convenience since no confusion should result in the development that follows.

SOLUTION OF EQUATIONS

There exists at present no method of obtaining an analytical solution to Equations (24) to (27) for a general diffusivity-concentration functional relationship. Indeed, we are not aware of any exact solutions of the above nonlinear diffusion equation for finite slabs. There do exist solutions (*10*, *14*) for specific diffusivity-concentration relationships for semi-infinite media, but these are very special and of limited use in analyzing the entire sorption curve. Hence, any solution of the equations governing the sorption process will necessarily be of approximate nature. A convenient method of obtaining approximate analytical solutions to nonlinear differential equations not readily handled by perturbation series is the method of weighted residuals. The weighted residual approach has been used with success in solving a variety of important problems, including boundary-layer flows and nonlinear heat and mass transfer phenomena. Fujita and Kishimoto (*5*) applied a weighted residual solution of the nonlinear diffusion equation for a semi-infinite medium to the analysis of sorption data, but their approach is much more limited than the method proposed here.

Good reviews of weighted residual methods have been given by Ames (*15*) and by Finlayson and Scriven (*16*). Basically, the method consists of formulating a solution of the problem which satisfies the partial differential equation, and perhaps some of the boundary conditions, only in some average sense over the region of interest rather than at each and every point of the region as is required of an exact solution. Thus, to obtain an approximate analytical solution to the sorption problem, we define a residual

$$R = \frac{\partial q_I}{\partial t} - \frac{\partial}{\partial \xi}\left[\frac{F(q_I)}{D_0}\,\frac{\partial q_I}{\partial \xi}\right] \tag{29}$$

and demand that

$$\int_0^1 W_k R \, d\xi = 0, \quad k = 1, 2, \cdots, n \tag{30}$$

where the W_k are weighting functions. By choosing an appropriate set of trial functions for $q_I(\xi, t)$, we can obtain an approximate solution which, in principle, approaches the exact solution as the number of functions in the expression for $q_I(\xi, t)$ becomes large.

In the present work we choose the weighting functions to be members of the complete set $(1, \xi, \xi^2, \cdots)$ so that the technique used here is what is usually referred to as the method of moments. From Equations (29) and (30) with $W_k = 1$, it follows that calculation of the zero moment gives

$$\frac{d}{dt}\left(\frac{M_I}{M_{I\infty}}\right) = \frac{F(1)}{D_0}\left(\frac{\partial q_I}{\partial \xi}\right)_{\xi=1} \tag{31}$$

Similarly, from Equations (29) and (30) with $W_k = \xi$, it can be shown that the first moment equation yields

$$\frac{d}{dt}\int_0^1 \int_0^\xi q_I \, d\xi' \, d\xi = \int_{\psi(t)}^1 \frac{F(q_I)}{D_0} \, dq_I \tag{32}$$

with

$$q_I(0, t) = \psi(t) \tag{33}$$

Higher moments were not calculated, partly because of the increased difficulty of the calculations and partly because the accuracy of a two-term approximate solution proved adequate.

A two-term trial solution of the form

$$\frac{q_I - \psi}{1 - \psi} = \left(\frac{\hat{m}_I}{\hat{M}_I}\right)^{2/3}\left[A_0 + A_1\left(\frac{\hat{m}_I}{\hat{M}_I}\right)^{1/3}\right] \tag{34}$$

is convenient for use in the present analysis where the $A_i(t)$ are the undetermined functions and where

$$\hat{m}_I = \int_0^\xi [q_I(\xi', t) - \psi(t)] \, d\xi' \tag{35}$$

$$\hat{M}_I = \int_0^1 [q_I(\xi', t) - \psi(t)] \, d\xi' \tag{36}$$

Close examination of Equation (34) reveals that it is capable of describing the concentration profile in the polymer phase over the entire time interval of the sorption experiment more accurately than any simple function of ξ because the $\hat{m}_I$ variable is representative of the amount of penetrant in a given part of the polymer sample. The surface boundary condition, Equation (26), is satisfied only if

$$A_0 + A_1 = 1 \tag{37}$$

and the physical requirement that concentrations be positive or zero everywhere in the polymer sheet places the following restriction on $A_0(t)$:

$$A_0 \geq 0 \tag{38}$$

In addition, Equation (34) satisfies Equation (25) identically and the initial condition, Equation (27), is satisfied by the trial solution since it can be shown that

$$\lim_{t \to 0}\left(\frac{\hat{m}_I}{\hat{M}_I}\right) = 0 \tag{39}$$

Substitution of Equation (34), the trial solution, into Equations (28) and (31) and use of the differential form of Equation (35) produce

$$\frac{M_I}{M_{I\infty}} = \hat{M}_I - \frac{3\hat{M}_I \psi \ln A_0}{(1 - A_0)(1 - \psi)} \tag{40}$$

$$\frac{d}{dt}\left(\frac{M_I}{M_{I\infty}}\right) = \frac{F(1)(1 - \psi)^2}{D_0 \hat{M}_I}\left(1 - \frac{A_0}{3}\right) \tag{41}$$

and an easy consequence of Equations (28) and (36) is

$$\hat{M}_I = \frac{M_I}{M_{I\infty}} - \psi \tag{42}$$

From Equations (40) and (42) an explicit expression for $\psi(t)$ can be derived for $A_0 > 0$:

$$\begin{aligned} \psi &= 0 && \text{if } 1 + \frac{3\sqrt{\Omega}\ln A_0}{1 - A_0} \geq 0 \\ \psi &= \frac{1 - A_0 + 3\sqrt{\Omega}\ln A_0}{1 - A_0 + 3\ln A_0} && \text{if } 1 + \frac{3\sqrt{\Omega}\ln A_0}{1 - A_0} < 0 \end{aligned} \tag{43}$$

where for convenience we let

$$\Omega = \left(\frac{M_I}{M_{I\infty}}\right)^2 \tag{44}$$

When $A_0 = 1$, Equation (43) assumes an indeterminate form which can be reduced to

$$\begin{aligned} \psi &= 0 && \text{if } 1 - 3\sqrt{\Omega} \geq 0 \\ \psi &= \frac{3\sqrt{\Omega} - 1}{2} && \text{if } 1 - 3\sqrt{\Omega} < 0 \end{aligned} \tag{45}$$

Furthermore, time differentiation of Equation (43) gives the result

$$\frac{d\psi}{dt} = E_1 \frac{d\Omega}{dt} + E_2 \frac{dA_0}{dt} \tag{46}$$

where for $A_0 > 0$

$$E_1 = \frac{3\psi \ln A_0}{2\sqrt{\Omega}(1 - A_0)\left[\dfrac{3(2\psi - \sqrt{\Omega})\ln A_0}{1 - A_0} + 2\psi - 1\right]} \tag{47}$$

$$E_2 = \frac{3\psi(\sqrt{\Omega} - \psi)(1 - A_0) + 3\psi A_0(\sqrt{\Omega} - \psi)\ln A_0}{A_0(1 - A_0)^2\left[\dfrac{3(2\psi - \sqrt{\Omega})\ln A_0}{1 - A_0} + 2\psi - 1\right]} \tag{48}$$

For $A_0 = 1$, the indeterminate forms of Equations (47) and (48) can be expressed as

$$E_1 = \frac{3\psi}{2\sqrt{\Omega}(1 + 4\psi - 3\sqrt{\Omega})} \tag{49}$$

$$E_2 = \frac{3\psi(\sqrt{\Omega} - \psi)}{2(3\sqrt{\Omega} - 4\psi - 1)} \tag{50}$$

Substitution of Equation (34) into Equation (32) and utilization of Equations (42) and (46) yield the following result for the first moment equation:

$$\frac{dA_0}{dt} = \frac{\displaystyle\int_\psi^1 \frac{F(q_I)}{D_0}\, dq_I - E_5 \frac{d\Omega}{dt}}{E_6} \tag{51}$$

where

$$E_3 = \frac{18A_0^2 - 11A_0^3 - 9A_0 + 2 + 6A_0^3 \ln A_0}{6(1 - A_0)^4} \tag{52}$$

$$E_4 = \frac{6A_0^3 \ln A_0 + 18A_0^2 \ln A_0 - 17A_0^3 + 9A_0^2 + 9A_0 - 1}{6(1 - A_0)^5} \tag{53}$$

$$E_5 = \frac{6E_3(1 - \psi)(\sqrt{\Omega} - \psi) + E_1(1 - \psi)^2\sqrt{\Omega}}{2(1 - \psi)^2\sqrt{\Omega}} + \frac{12E_1E_3\sqrt{\Omega}(\psi - \sqrt{\Omega}) + 6E_1E_3\sqrt{\Omega}(\Omega - \psi^2)}{2(1 - \psi)^2\sqrt{\Omega}} \tag{54}$$

$$E_6 = \frac{12E_2E_3(\psi - \sqrt{\Omega}) + 6E_2E_3(\Omega - \psi^2) + 6\hat{M}_I^2E_4(1 - \psi) + E_2(1 - \psi)^2}{2(1 - \psi)^2} \tag{55}$$

Also, it can easily be shown that

$$\lim_{A_0 \to 1} E_3 = \frac{1}{4} \tag{56}$$

$$\lim_{A_0 \to 1} E_4 = -\frac{1}{20} \tag{57}$$

Finally, from the above considerations it is possible to show that the following equations are also valid:

$$\Omega(0) = 0 \tag{58}$$

$$\psi(0) = 0 \tag{59}$$

$$\hat{M}_I(0) = 0 \tag{60}$$

$$\left(\frac{d\psi}{dt}\right)_{t=0} = 0 \tag{61}$$

$$\left(\frac{d\Omega}{dt}\right)_{t=0} = \frac{2F(1)\left[1 - \frac{A_0(0)}{3}\right]}{D_0} \tag{62}$$

$$\left(\frac{dA_0}{dt}\right)_{t=0} = 0 \tag{63}$$

$$\hat{M}_I(\infty) = 0 \tag{64}$$

It is clear that Equations (42), (43), (51), and a revised form of Equation (41)

$$\frac{d\Omega}{dt} = \frac{2F(1)(1 - \psi)^2\left(1 - \frac{A_0}{3}\right)}{D_0\left(1 - \frac{\psi}{\sqrt{\Omega}}\right)} \tag{65}$$

constitute a set of four equations, two algebraic and two differential, which can be solved for the four unknown time-dependent quantities, Ω, $\hat{M}_I$, ψ, and A_0, if the diffusivity-concentration relationship and the thermal equation of state are given and if the initial value of A_0 is known. From Equations (51) and (61) to (63) it is possible to deduce that $A_0(0)$ is a root of the following equation:

$$\frac{11A_0^4 - 51A_0^3 + 63A_0^2 - 29A_0 + 18A_0^3 \ln A_0 - 6A_0^4 \ln A_0 + 6}{3(1 - A_0)^4} = \int_0^1 \frac{F(q_I)}{F(1)}\, dq_I = I_0(A_0) \tag{66}$$

It is evident that

$$I_0(0) = 2 \tag{67}$$

$$I_0(1) = 1 \tag{68}$$

$$I_0(3) = 0 \tag{69}$$

and the functional dependence of $I_0(A_0)$ is depicted in Figure 1. Hence, if $F(q_I)$ is given, the initial value for A_0 follows immediately from Equation (66), and the direct problem can be solved by considering Equations (42), (43), (51), and (65) along with the appropriate initial conditions. It is apparent that the above weighted residual solution to the direct problem is not truly analytical, for we have merely reduced the partial differential equation to two highly nonlinear ordinary differential equations which must be solved by finite-difference methods. However, the solution of the inverse problem, that of deriving the concentration dependence of the diffusivity from sorption data, does not suffer the same shortcoming, since, in essence, only algebraic expressions relate the unknown quantities to the measured variables and their derivatives. The analytical

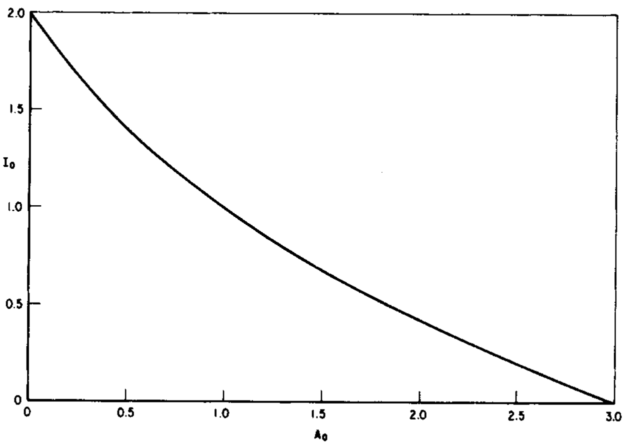

Fig. 1. Functional dependence of $I_0(A_0)$.

solution to the inverse problem and its utilization in the analysis of sorption data are discussed in the next section.

We conclude this section by considering what the equations from the weighted residual method predict for long times. In the long-time limit it is possible to derive from Equation (65) the expression

$$\lim_{t\to\infty}\left[\frac{d\ln(1-\sqrt{\Omega})}{dt}\right] = \frac{3F(1)\,[\ln A_0(\infty)]^2\,[3-A_0(\infty)]}{D_0[3\ln A_0(\infty)+1-A_0(\infty)]\,[1-A_0(\infty)]} \tag{70}$$

and from an asymptotic form of Equation (51) it follows that $A_0(\infty)$ is a root of the following equation:

$$\frac{5A_0^4-27A_0^3+27A_0^2-5A_0}{2(1-A_0)^3(3\ln A_0+1-A_0)} + \frac{\ln A_0(-6A_0^4+36A_0^3-54A_0^2+54A_0-18)}{2(1-A_0)^3(3\ln A_0+1-A_0)} + \frac{(\ln A_0)^2(9A_0^3-45A_0^2+63A_0-27)}{2(1-A_0)^3(3\ln A_0+1-A_0)} = 0 \tag{71}$$

The only physically meaningful root of Equation (71) can be shown to be

$$A_0(\infty) = 1.24756 \tag{72}$$

and hence Equation (70) can be rewritten as

$$\lim_{t\to\infty}\left[\frac{d\ln(1-\sqrt{\Omega})}{dt}\right] = -\frac{2.4975\,F(1)}{D_0} \tag{73}$$

The asymptotic behavior of the exact solution of Equations (24) to (27) is such that the solution predicts

$$\lim_{t\to\infty}\left[\frac{d\ln(1-\sqrt{\Omega})}{dt}\right] = -\frac{\pi^2F(1)}{4D_0} \approx -\frac{2.4674\,F(1)}{D_0} \tag{74}$$

Comparison of Equations (73) and (74) provides an estimate of the accuracy of the weighted residual method in the long-time limit.

APPLICATION OF METHOD

The approximate analytical solution presented in the previous section is used as the basis for the following method of obtaining the concentration dependence of the diffusivity from sorption data:

1. Determine Ω and $d\Omega/dt$ as functions of time from sorption data.
2. Use the long-time sorption data to evaluate $F(1)$ using Equation (74).
3. Employing the Ω and $d\Omega/dt$ data along with $F(1)$, solve the set of algebraic Equations (42), (43), and (65) for ψ, $\hat{M}_I$, and A_0 as functions of time. At $t = 0$, Equation (62) replaces Equation (65).
4. Use the results of steps 1 to 3 to obtain

$$\int_{\psi}^{1}\frac{F(q_I)}{D_0}\,dq_I$$

as a function of ψ from Equation (51). At $t = 0$, $\int_0^1 \frac{F(q_I)}{D_0}\,dq_I$ can be calculated from Equation (66).

5. Numerically differentiate the integral obtained in step 4 to determine $F(q_I)$ as a function of q_I.
6. Utilize the thermal equation of state to determine D as a function of ρ_I.

It is clear from the previous development that the quantities D_0 and $\hat{V}_J^0$ which appear in the equations employed in the above method are arbitrary constants which are introduced only to present the equations in dimensionless form. Since this method of analysis merely involves the solution of algebraic equations, it does not require elaborate computation and can readily be applied to the analysis of both absorption and desorption data. Experimental errors in sorption data obtained near the final equilibrium point can sometimes be significant, but Frensdorff (*11*) has shown that with care adequate accuracy can be obtained for data taken during the long-time portion of the experiment.

To test this proposed method for analyzing sorption data without the complications associated with experimental measurements, theoretical Ω versus time points were obtained from a numerical solution of Equations (24) to (28) which describe the sorption process. The application of implicit finite-difference techniques (*15*) to these equations is straightforward and therefore the details are not presented. Convergence of the finite-difference solutions to the solutions of the partial differential equation was established in the usual manner by varying the mesh sizes for the distance and time variables. Sets of test data points were obtained for several cases for which the diffusivity is an exponential function of the concentration of the penetrant. An approximate exponential dependence has been observed for many penetrant-polymer systems (*8*, *9*, *17*), and this highly nonlinear dependence should provide a severe test of the proposed method of analysis. Comparison of the diffusivity-concentration relationship calculated from the test data using the method outlined above with the original diffusivity function which was used to generate the test sorption data permits a direct evaluation of this technique. In essence, we wish to determine the conditions under which the weighted residual solution to the inverse problem provides a satisfactory approximation to an exact analysis.

Two examples of the accuracy of the method are presented in Table 1 where $F(q_I)$ is treated as the diffusivity to avoid introducing a thermal equation of state. In both cases the number of numerically generated data points used was less than the amount that can easily be obtained in a typical sorption experiment. For case I, the diffusivity increases by a factor of 5 and the proposed method of analysis yields a diffusion coefficient which is correct to about 5% for 85% of the concentration range. Case II.provides an example of a diffusion coefficient which decreases by a factor of 3 over the concentration range studied. For this case 5% accuracy is achieved for approximately 80% of the concentration range. In all examples studied, the accuracy of the derived diffusion coefficients was better for concentrations near the equilibrium concentration. In addition, as would be expected, the accuracy of the method decreases as the range of diffusivity for the sorption run, and hence the nonlinearity, increases.

The above examples establish the accuracy to be expected when dealing with diffusion coefficients which are exponential functions of concentration. It is known (*10*) that the accuracy of a weighted residual method is dependent on the form of the concentration dependence of the diffusion coefficient and, hence, the above results do not necessarily imply equivalent accuracy for another diffusivity-concentration functional relationship. However, the exponential relationship provides an example of as severe a nonlinearity as can be expected under realistic physical circumstances, and the accuracy for other functional relationships for the diffusivity (such as a linear concentration dependence) is very probably better. Thus, the above results indicate that the present method gives 5% accuracy in analyzing a general sorption curve for at least 80% of the concentration range for diffusion coefficients increasing by a factor of 5 and decreasing by a factor of 3. These ranges could conceivably be increased by using a better trial function.

The proposed method makes it possible to analyze a single sorption curve for the determination of the concentration dependence of the diffusion coefficient over at least 80% of

TABLE 1. RESULTS OF ANALYSIS OF TEST DATA

Case I. $F(q_I) = D_0 \exp(1.61\, q_I)$

q_I	$F(q_I)/D_0$	Calculated $F(q_I)/D_0$	% Error in calculated $F(q_I)/D_0$
0	1.000	0.699	30.1
0.05	1.084	0.867	20.0
0.10	1.175	1.036	11.8
0.15	1.273	1.204	5.4
0.21	1.392	1.390	0.1
0.24	1.466	1.498	2.2
0.30	1.620	1.707	5.4
0.41	1.948	2.044	4.9
0.52	2.293	2.303	0.4
0.60	2.640	2.617	0.8
0.71	3.135	3.092	1.3
0.80	3.637	3.579	1.6
0.90	4.262	4.183	1.9
0.95	4.553	4.465	1.9

Case II. $F(q_I) = D_0 \exp(-1.10\, q_I)$

q_I	$F(q_I)/D_0$	Calculated $F(q_I)/D_0$	% Error in calculated $F(q_I)/D_0$
0	1.000	1.347	34.7
0.06	0.940	1.204	28.1
0.10	0.895	1.048	17.1
0.15	0.851	0.920	8.1
0.20	0.802	0.845	5.2
0.25	0.760	0.791	4.1
0.30	0.716	0.739	3.2
0.40	0.645	0.658	1.9
0.50	0.576	0.579	0.6
0.60	0.516	0.515	0.2
0.70	0.463	0.459	0.7
0.80	0.413	0.409	1.1
0.90	0.371	0.367	1.2
0.95	0.351	0.356	1.4

the concentration interval. The method handles both reverting and progressing experiments, the entire sorption curve can be used, no diffusion coefficient-concentration relationship is assumed, and volume change on mixing and phase volume change are taken care of automatically. However, there are basically two shortcomings of the proposed technique. First of all, the method requires the utilization of numerical differentiation in the data analysis. This limitation is relatively minor since many data points are readily available for the differentiation steps, unlike previous methods where a significant amount of labor must be expended to generate a sufficient number of points for accurate numerical differentiation. In addition, in order to obtain accurate results for some penetrant-polymer systems it may be necessary to perform a series of experiments to cover a large concentration range. However, this requirement is not too restrictive if one considers that the analysis of four absorption runs in series could accurately establish the concentration dependence of a diffusion coefficient which varies by a factor of 625. Hence, even for large changes in the diffusivity, a relatively few experiments are required to obtain accurate results.

It is evident from Table 1 that accurate results cannot be obtained for the entire concentration range from the analysis of one sorption curve. However, by the analysis of consecutive absorption and desorption experiments, accurate values of $F(q_I)$ and thus D can be determined for the complete concentration range since the absorption data will give accurate values of D at the high values of ρ_I and the desorption data will yield accurate results at the low values of ρ_I.

A wide variety of trial solutions could, of course, be used to implement the scheme proposed above. One possibility would be the solution proposed by Fujita and reported by Crank (*10*). The trial solution selected here was chosen from examination of the shapes and features of calculated concentration-distance curves for a variety of diffusivity-concentration relationships; this was done to incorporate as much accuracy into the trial solution as possible. This trial solution has the unique feature that a single expression uniformly accurate for all stages of the sorption process is used instead of the usual two expressions. In addition, the uniqueness problem inherent in some weighted residual solutions, such as that of Fujita, is avoided here.

NOTATION

A_0, A_1 = time-dependent coefficients in trial function
D = binary diffusion coefficient
D_0 = arbitrary reference diffusion coefficient
E_1 to E_6 = quantities defined by Equations (47) to (50) and (52) to (57)
$F(q_I)$ = quantity defined by Equation (12)
I_0 = integral defined by Equation (66)
j_I = mass diffusion flux of component I relative to mass average velocity
j_I° = mass diffusion flux of component I relative to velocity of component J
L = initial thickness of binary phase
M_I = total amount of component I which has entered binary phase at time t
$M_{I\infty}$ = total amount of component I which has entered binary phase at infinite time
$\hat{M}_I$ = variable defined by Equation (36)
$\hat{m}_I$ = variable defined by Equation (35)
q_I = concentration variable defined by Equation (5)
q_{IE} = value of q_I at surface of finite phase
q_{IO} = initial value of q_I
t = time
$\hat{V}_J^{\circ}$ = arbitrary reference partial specific volume of component J
v_I = velocity of component I
X = instantaneous thickness of binary phase
x = distance variable in direction of diffusion

Greek Letters

ξ = length variable defined by Equation (6)
ξ_L = quantity defined by Equation (16)
ρ = total density of binary phase
ρ_I = mass density of component I
ρ_{IE} = equilibrium mass density of component I
ρ_{IO} = initial mass density of component I
ψ = quantity defined by Equation (33)
Ω = quantity defined by Equation (44)
ω_I = mass fraction of component I

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