

General theory for determination of diffusion coefficients of solvents and gases in polymers

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A general measurement theory for determining the diffusion coefficient D of small molecules in polymer matrices is presented. This theory is applied to an arbitrary geometry of the polymer sample and an arbitrary initial penetrant content in the polymer. It is shown that one does not need to know specifically the dependence of the measured quantity on the concentration of the diffusing species, nor does one need to measure the equilibrium state of the system. By determining the differences ΔM of a measured quantity M , which may be spectroscopic absorption, weight increase or any other concentration-dependent quantity, as a function of time, the diffusion coefficient can be determined. The theory was tested with the results of water diffusion into polyacrylonitrile and poly(vinyl toluene). Diffusion coefficients determined with the general theory agree well with the results achieved by using more complicated conventional calculations. The benefits of the use of the general measurement theory are that one can simplify both measurements and calculations.

(Keywords: diffusion coefficients; small molecules; measurement theory)

BACKGROUND

One-dimensional Fickian diffusion is described by the differential equation:

$$\partial C / \partial t = D \partial^2 C / \partial z^2 \quad (1)$$

where C is the concentration of the diffusing species, D the diffusion coefficient and z the direction of diffusion. Equation (1) is readily solved when the boundary and initial conditions are known. The diffusion geometry most often used in polymers is a thin film^{1,2}. The book by Crank³ contains several example solutions $C(z,t)$, which are typically infinite sine or cosine series for a long-time solution.

The measured quantity in diffusion experiments in polymers is seldom the concentration distribution $C(z,t)$ but an integrated mass increase M_t (see e.g. Schlotter and Furlan² and references therein) or absorption A_t of i.r. light¹. These solutions assume a known initial concentration of the diffusing species in the polymer and sometimes also a known concentration of the diffusing species outside the polymer. In addition, the determination of D requires also the measurement of the equilibrium mass increase M_∞ (or equilibrium absorbance A_∞). These are often tedious and time-consuming to measure.

In this work a general theory for the measurement of the diffusion coefficient of a penetrant in polymers (or basically in any other medium) is presented. It is shown how the theory can be applied to different possible specimen geometries. The long-time solution of the diffusion equation is simplified to finding the eigenvalues for a differential equation of the second order. Because the eigenvalues of the diffusion equation depend only on

the geometry, the initial concentration distribution of the diffusing species can be arbitrary. The diffusion coefficient can be calculated by knowing the first eigenvalue. That makes measurements much easier to perform than in the short-time solution of the diffusion equation.

The diffusion equation is first solved in a general case and it will then be applied to typical specific geometries that are used in experiments. It is supposed that there will be no swelling caused by diffusion. If that is not the case, then the swelling must be taken into account as described by Kirkwood *et al.*⁴.

THEORETICAL PART

Let us suppose that penetrant molecules, which are diffusing into or out of a polymer specimen, are surrounding the specimen of an arbitrary three-dimensional shape. In this work diffusion is supposed to be Fickian with a constant diffusion coefficient D . If D is not constant, the measured data do not approach the straight line presented below (cf. equation (14) and Figure 1). In that case one may vary the initial and outer concentrations of the diffusing species and from the change of the calculated D estimate the true D . The diffusion equation is:

$$\partial C / \partial t = D \nabla^2 C \quad (2)$$

In a general three-dimensional case the initial and boundary conditions are⁵:

$$C = C(r,0) \quad t=0 \quad (3)$$

$$\alpha C|_S + \beta \partial C / \partial n|_S = 0 \quad t>0 \quad (4)$$

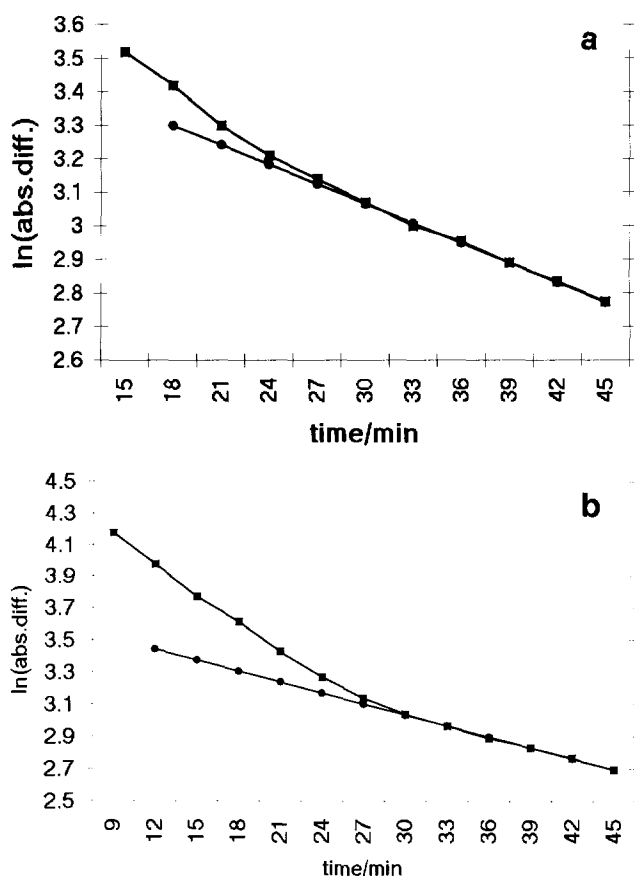


Figure 1 Logarithm of the differences of integrated absorbance versus time for the system water-PAN at 23°C: sample prepared (a) at 92°C and (b) at 57°C. Absorbance is taken in arbitrary units. $\Delta t = 30$ min for ΔM calculation. Raw data have been taken from figure 9 in ref. 1. Squares are experimental points and the least-squares lines are marked with full circles

In equation (4) the notation $|_S$ means the value on the surface. Equation (4) takes into account that the diffusion specimen may have open and/or closed parts on its surface S . The partial differential in equation (4) is taken in the direction of the outer normal n , α and β are space-dependent functions, and r is a general space coordinate.

By applying the method for the separation of variables, i.e. by writing $C = R(r)T(t)$, one can solve the differential equation (4) with the result^{5,6}:

$$C(r, t) = a_0 + \sum_{i=1}^{\infty} a_i R_i(r) \exp(-\lambda_i D t) \quad (5)$$

where λ_i is the eigenvalue corresponding to the eigenfunction R_i . For solving the space-dependent part we apply typically Fourier sine (cosine) and Bessel series. The coefficients a_i are determined from the equation:

$$C(r, 0) = \sum_{i=0}^{\infty} a_i R_i \quad (6)$$

by using the orthogonal properties of the eigenfunctions. Specifically, the first coefficient ($i = 0$) is:

$$a_0 = V^{-1} \int_V C(r, 0) dV = C_{\infty} \quad (7)$$

In equation (7) C_{∞} is the equilibrium concentration of the penetrant in the specimen after infinite time and V is the volume of the specimen.

During an experiment the sample is connected to a measurement system, which is assumed to have a time-independent measurement functional $F(C(r)) = F(r)$. The measured property of the specimen at time t is derived from equation (5) as follows:

$$M(t) = \int_V F(r) C(r, t) dV \quad (8)$$

where $M(t)$ is the measured quantity, e.g. the mass increase (loss) or absorption of i.r. radiation. $F(r)$ describes how individual points of the specimen affect the overall quantity $M(t)$ of the specimen.

For solving equation (8) it is assumed that measuring functional F is linear and homogeneous or that in a non-linear case a small enough concentration interval ΔC is used so that the following approximation is valid⁷:

$$F'(C + \Delta C) \approx F'(C) + F(\Delta C) \quad (9)$$

where F' is a non-linear functional and F a linear homogeneous functional. The term $F(\Delta C)$ in equation (9) then replaces $F(r)$ in the integral term of equation (12) below.

By combining equations (5)–(8) one gets:

$$M(t) = M_{\infty} + \sum_{i=1}^{\infty} M_i \exp(-\lambda_i D t) \quad (10)$$

where

$$M_{\infty} = a_0 \int_V F(r) dV \quad (11)$$

$$M_i = a_i \int_V F(r) R_i(r) dV \quad (12)$$

M_{∞} is the equilibrium value of $M(t)$ after infinite time.

The eigenvalues λ_i increase rapidly for any region with the index i . Therefore, after a certain time, which depends on the geometry of the specimen, the first term in the sum of equation (10) predominates. If we measure the equilibrium value M_{∞} , we can then determine the diffusion coefficient D with a known specimen geometry (λ_1 known) from the following linear expression:

$$\ln[M_{\infty} - M(t)] = -\lambda_1 D t + \ln M_1 \quad t > t' \quad (13)$$

where t' is a geometry-dependent time required to make the terms in equation (10) with $i > 1$ vanishingly small compared to the first term.

Depending on the dimensions of the diffusion specimen it takes a long time (hours, days or weeks) to measure M_{∞} . Therefore, the measured data may be treated using the so-called Guggenheim's elimination method, which eliminates the need for an M_{∞} value. For that purpose we take differences $\Delta M(t) = M(t + \Delta t) - M(t)$ in equation (10) with only the first term of the sum taken into account. The result can be expressed as:

$$\ln[\Delta M(t)] = -\lambda_1 D t + \text{constant} \quad t > t' \quad (14)$$

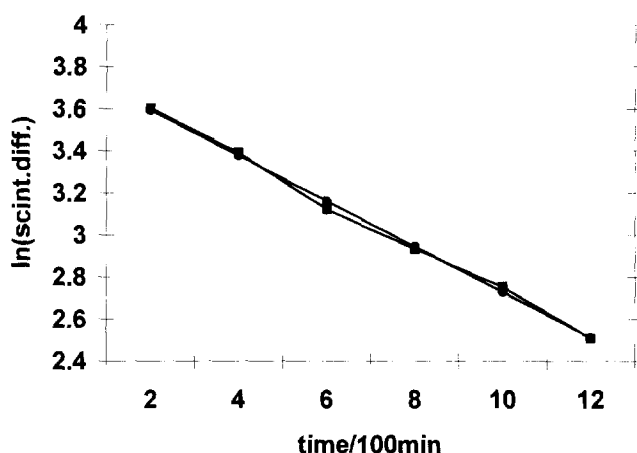


Figure 2 Logarithm of the differences of scintillation-monitored water uptake by poly(vinyl toluene) versus time. Intensity is taken in arbitrary units. $\Delta t = 600$ min for ΔM calculation. Raw data have been taken from figure 2 in ref. 10. Squares are experimental points and the least-squares line is marked with full circles

where constant $= \ln\{a_1[\exp(-\lambda_1 D \Delta t) + 1]\}$. The interval Δt is chosen so that the differences $\Delta M(t)$ are large enough and at the same time the number of points remains adequate for good statistics.

It is important to note that in the derivation of equations (13) and (14) an arbitrary initial concentration distribution of the diffusing species in the specimen was supposed. Another point to note is that the measuring functional $F(r)$ and the boundary conditions, i.e. the outer concentration of the diffusing species, are also arbitrary. As it turns out in the following, the only thing we need to know from our specimen is the geometry, i.e. the dimensions and how the closed and open surfaces are located. Even that is typically reduced to the need to know the smallest dimension of the specimen, i.e. the thickness. All this means that the method simplifies tremendously the diffusion coefficient measurement.

Some practical specimen geometries

There are a number of possible diffusion geometries for which there exist ready solutions^{3,8}. Let us start with a very common geometry, a rectangular box with edges a , b and c ($a \approx b \approx c$). The first eigenvalue is as follows for four variations of open and closed surfaces: $\lambda_1 = (\pi/a)^2 + (\pi/b)^2 + (\pi/c)^2$ for all surfaces open to the penetrant; $\lambda_1 = (\pi/a)^2 + (\pi/b)^2$ for ab surfaces closed to the penetrant and other surfaces open; $\lambda_1 = (\pi/2a)^2 + (\pi/b)^2$ for ab surfaces and one bc surface closed to the penetrant and other surfaces open; and $\lambda_1 = (\pi/2a)^2$ for all other surfaces closed but one bc surface open to the penetrant.

If the thickness a of the specimen gets much smaller than the other dimensions (i.e. $a \ll b, c$), the first eigenvalue $\lambda_1 = (\pi/a)^2$ for the case when both of the bc surfaces are open. However, if only one bc surface is open and the other is closed, then $\lambda_1 = (\pi/2a)^2$. In the work by Fieldson and Barbari¹ this was the case ($a = L$).

Another common specimen geometry is the cylinder. There the most common measurement arrangement is that both ends are closed and the surface of the rod is open to the diffusing substance. Then $\lambda_1 = (2.405/r)^2$ where r is the radius of the cylinder. This λ_1 is found from the first zero of the Bessel function of the first kind,

of zero order⁹: $J_0(2.405) = 0$. If the cylinder shrinks to a disc with thickness a and diameter $2r$, and one of the flat surfaces is open to the penetrant, then $\lambda_1 = (\pi/2a)^2$.

RESULTS

As an example for the applicability of the measurement theory, water diffusion in polyacrylonitrile (PAN) at 23°C measured by Fieldson and Barbari¹ was chosen. They used FTi.r. spectroscopy in a.t.r. mode for detecting *in situ* water penetration into PAN films of thickness of ca. 7.5 μm . From figure 9 in their publication, two absorbance curves for films prepared at 57 and 92°C were arbitrarily chosen. From the curves, absorbances were measured every 3 min in arbitrary units and differences ΔM in equation (14) at 30 min intervals were taken. The results are plotted in Figure 1.

The least-squares fitting gives (with 99% confidence interval) the straight lines:

$$\begin{aligned} \ln[\Delta M(t)] = & \\ & -(2.267 \pm 0.080) \times 10^{-2} t/\text{min} + (3.715 \pm 0.031) \quad (92^\circ\text{C}) \end{aligned}$$

$$\begin{aligned} \ln[\Delta M(t)] = & \\ & -(1.952 \pm 0.075) \times 10^{-2} t/\text{min} + (3.652 \pm 0.029) \quad (57^\circ\text{C}) \end{aligned}$$

From the slopes of the lines [slope $= -(\pi/2a)^2 D$] and the thickness of the sample $a = 7.5 \mu\text{m}$, one gets the values for the diffusion coefficient:

$$D = (8.61 \pm 0.31) \times 10^{-11} \text{ cm}^2 \text{ s}^{-1} \quad (92^\circ\text{C})$$

$$D = (7.41 \pm 0.29) \times 10^{-11} \text{ cm}^2 \text{ s}^{-1} \quad (57^\circ\text{C})$$

The corresponding values calculated by Fieldson and Barbari¹ by using the measured A_∞ value, known initial concentration distribution and known measuring functional (the decay E of the evanescent wave in the polymer) are:

$$D = (8.51 \pm 0.31) \times 10^{-11} \text{ cm}^2 \text{ s}^{-1} \quad (92^\circ\text{C})$$

$$D = (7.58 \pm 0.37) \times 10^{-11} \text{ cm}^2 \text{ s}^{-1} \quad (57^\circ\text{C})$$

Another example of the applicability of the theory is the measurement of water diffusion in poly(vinyl toluene) film by Krongauz and Reddy¹⁰. They used tritium-labelled water for the detection of the diffusion. Their results, presented in the form of equation (14), are depicted in Figure 2.

The least-squares fitting gives (with 99% confidence interval) the straight line:

$$\ln[\Delta I(t)] = -(1.080 \pm 0.050) \times 10^{-3} t/\text{min} + (3.809 \pm 0.040)$$

From the slope of the line and from the first eigenvalue $\lambda_1 = (\pi/a)^2$ with $a = 0.125$ inch (0.318 cm) one gets $D = (1.84 \pm 0.10) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. This agrees quite well with the value $1.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ given in the paper (the confidence interval is not given).

DISCUSSION

The results obtained with the general method agree well with the results given in the original publications and calculated by using much more information from the original experiments. It is thus proven that the general measurement theory works. Its use can be extended to any kind of diffusion measurements in polymers when the measured property is directly related to the concentration of the diffusing species. The method is applicable only for the long-time solution of the diffusion equation. The experimental points approach, as is also seen in *Figure 1*, the straight line from above.

The benefits of the theory are obvious: (a) We do not need to know experimental conditions as accurately as has been the case previously. (b) We can use many kinds of diffusion geometries according to what is most desirable for us. (c) We do not need to measure the initial and equilibrium concentrations of the diffusing species. (d) The method can be applied to all kinds of measured quantities, like absorption of different kinds of spectroscopic radiation, electrical conductivity, mass increase of the diffusion specimen and radiation of radioactive tracers. One further generalization of the theory is that the geometry of the diffusion specimen may be totally unknown. Then the geometry is calibrated with penetrant diffusion of known D by using the fact that the slope of the straight part in equation (14) is $\lambda_1 D$.

The drawbacks of the theory are as follows: (a) We have to disregard first measured values, which would give much greater differences and thus better accuracy. (b) By taking small differences between large numbers, the scatter of the points increases substantially. (c) By taking differences, the number of experimental points for the determination of the diffusion coefficient is substantially reduced. To some extent one can overcome these drawbacks by using optimal initial conditions and/or optimal measuring functionals⁷. Also, a simpler method encourages researchers to make more experiments and

then the statistics of the measurements will narrow the error limits. Another way to proceed is to use more than one term from the infinite series in equation (10). This has been proven in the case of tracer diffusion¹¹. Then one has more than two parameters to be fitted in the non-linear least-squares method, but with computers that is not an obstacle.

If the diffusion coefficient is dependent on the concentration, the determined value is an average within the concentration range in the experiment.

CONCLUSIONS

The results presented in this work demonstrate that the determination of the small-molecule diffusion in polymers can be done in a very simple way. It allows use of nearly any kind of measurement of a variable dependent on the concentration of the diffusing species. Thus, it should open cheap and easy ways to determine small-molecule diffusion in polymers.

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