REFERENCES

1. E.D. Mullen, J.A. Ritter, J. AWWA 66(1974): p. 473.
2. R.A. Ryder, J. AWWA, 72(1980): p. 267.
3. U.S. EPA Proposed Regulations to Control Lead in Drinking Water, Federal Register, Aug. 18, 1988.
4. M.R. Schock, C.H. Neff, "Chemical Aspects of Internal Corrosion: Theory, Prediction and Monitoring," Proceedings of the 11th AWWA Water Quality Technology Conference, in Nashville, 1982.
5. ASTM D2688-83 method B, Coupon Test (Philadelphia, PA: American Society for Testing and Materials [ASTM], 1983).
6. ASTM D2688-83 method C, Machined Nipple Test (Philadelphia, PA: ASTM, 1983).
7. E. Heitz, W. Shwenk, Brit. Corro. J. 11(1976): p. 74.
8. C. Wagner, Z. Traud, J. Electrochem. Soc. 44(1938): p. 391.
9. J.A.V. Butler, Trans. Faraday Soc. 17(1924): p. 734.
10. J. Tafel, J. Physik Chem. 50(1904): p. 641.
11. W.J. Weber, Jr., Physiochemical Processes for Water Quality Control, Chapter 10 (New York, NY: Wiley Interscience, 1972).
12. M. Stern, A.L. Geary, J. Electrochem. Soc. 104(1957): p. 56.
13. S.H. Reiber, J.F. Ferguson, M.M. Benjamin, J. AWWA 80(1988): p. 41.
14. H.H. Uhlig, Corrosion and Corrosion Control (New York, NY: John Wiley and Sons, 1971).
15. Internal Corrosion of Water Distribution Systems, Chapter 3—Corrosion of Galvanized Pipe (Denver, CO: AWWA, 1985).
16. H.S. Reiber, J.F. Ferguson, M.M. Benjamin, J. AWWA 79(1987): p. 71.
17. S.C. Dexter, L.N. Moettus, K.E. Lucas, Corrosion 41(1985): p. 598.
18. W.W. Frenier, F.B. Growcock, Corrosion 40(1984): p. 663.
19. F.P. Ijsseling, Brit. Corro. J. 21(1986): p. 95.
20. ASTM G5-82, Standard Reference Method of Making Potentiostatic Polarization Measurements (Philadelphia, PA: ASTM, 1982).
21. M.J. Danielson, Corrosion 38(1982): p. 580.
22. J. Jankowski, R. Juchniewicz, Corro. Sci. 20(1980): p. 841.
23. S.M. Gerchakov, L.R. Udey, F. Mansfeld, Corrosion 37(1981): p. 696.
24. R.L. Leroy, Corrosion 31(1975): p. 173.
25. R. Grauer, P.J. Moreland, G. Pini, A Literature Review of Polarization Resistance Constant Values (Houston, TX: NACE, 1982).

APPENDIX A

Nomenclature

β_a	= Anodic Tafel slope (mV/decade of polarization current)
β_c	= Cathodic Tafel slope (mV/decade of polarization current)
E^o	= Standard oxidation potentials
E_{corr}	= Freely corroding surface potential (V)
E	= Electrode potentials (V)
F	= Faraday's constant (coul/g-equiv)
i	= Applied current density impressed upon the test electrode surface (Amps/cm^2)
i_o	= Equilibrium exchange current or corrosion current density (A/cm^2)
$i_{(oxidation)}$	= Partial anodic current generated from the oxidation of metal m to m^+
$i_{(reduction)}$	= Partial cathodic current generated from the reduction of substance z
λ	= Charge transfer coefficient (dimensionless)
n	= Electron transfer equivalents
η	= Polarization offset or overvoltage (V)
R	= Universal gas constant ($mL^2 \cdot T^{-2}$)
R_p	= Polarization resistance (dV/dI at E_{corr})
T	= Temperature (K)

Sorption/Diffusion Prediction in Nonmetallics Using Fick's Law☆

*E.M. Rosen and D.C. Silverman**

ABSTRACT

Rapid evaluation of nonmetallic materials to predict long-term absorption, diffusion, and permeation properties in corrosive service remains an elusive goal in materials engineering. A number of efforts have been reported that have used various forms of the analytical solution to the diffusion equation to make lifetime predictions from mass change measurements. This paper explores the limitations of three approaches for making these predictions. The analysis is limited to absorption with no simultaneous desorption from the nonmetallic material. Consideration of the dimensionless group Dt/l^2 is important in deciding on the appropriate sample thickness and test time. The results of this evaluation indicate that some results reported in the literature are incorrect.

KEY WORDS: absorption, corrosion, degradation, diffusion, Fick's laws, linings, nonmetallic materials, permeation, plastic, polymers, rubbers

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INTRODUCTION

Nonmetallic materials such as plastics and rubbers are widely used as materials of construction in the process industries. Their prevalence is created by their ability to withstand some environments better and at lower cost than metallic competitors. They can function as sheet linings or as stand-alone materials for containment among other applications. Their use is widely documented.[1]

Choice of which plastic or rubber to use in an application often requires assessment of its behavior in the desired environment. This assessment usually involves exposure of the nonmetallic to the environment for some period of time and then evaluation of the exposed sample for changes in physical properties. An example of a standardized test is given by ASTM[(1)] D-471 for evaluating rubber materials.[2] Tests derived from the standardized immersion test have been applied to a large number of rubbers and plastics. Usually, a number of physical properties are evaluated at predetermined intervals. Judgment is made on the expected long-term behavior from the effects of the environment on changes in mass (weight), volume, hardness, and strength of the tested mate-

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rial. The need for protracted test times can sometimes pose a problem in that some materials may require test times of 90 or 180 days and the answer is required sooner. This need has been a driving force for development of accelerated tests for predicting the long-term behavior of these types of materials.

Two properties that can affect usefulness of a nonmetallic material are the rate at which the contained environment can migrate through the material and the amount of the migrating material that absorbs into it. For a material to be useful, both the rate of migration through and the amount of absorption into the nonmetallic after long times must be small. Otherwise, the contained fluid would reach the outside environment and the containment vessel might fail because of loss of strength. The capability of predicting these properties from simple immersion tests has been pursued by a number of workers.

In addition, the lifetime of a lining material might depend on how rapidly the environment will permeate through it to attack the metal–lining bond. Information on the time to affect this bond requires knowledge of the rate of permeation through the material. This permeation rate is related to the diffusion rate and the solubility in the nonmetallic material. In fact, when the diffusion coefficient is independent of concentration, and the concentration of the absorbing species in the nonmetallic is directly proportional to its concentration in the external environment (the sorption isotherm is linear), the permeation coefficient becomes, simply, the product of the diffusion coefficient times the solubility.[3,4] This relationship assumes that the absorption and desorption processes between the liquid and lining membrane are rapid so that an equilibrium is established quickly at the interface between them.

This relationship among permeation, diffusion, and solubility means that the ability of a contained liquid or its components to permeate through plastics and rubbers might be quantified by determining the diffusion coefficient and solubility of the medium in the plastic or rubber without running a separate permeation test. Since relatively fast performance predictions are often required, accelerated tests that can be designed to provide the necessary data have been desired. This need has led a number of workers to explore how diffusion coefficients and equilibrium concentrations might be estimated rapidly using nonmetallic samples taken from the same base-stock as would be used to construct the actual lining or containment vessel.

Reports on designing such experiments and then using the results to estimate diffusion coefficients and concentrations at infinite time (equilibrium concentrations) for corrosion predictions have usually started with the assumption that Fick's laws can be used to model the diffusion process. The experiment has been constructed so that some form of the analytical solution to Fick's second law could be used to make predictions. The full solution to Fick's second law is an infinite sum of terms of decreasing magnitude.[3] The attempts to apply this solution have focused on either of two approaches. The first is to use the first exponential term of the infinite sum in the complete analytical solution. The second is to use the solution derived from the Boltzmann transformation of the independent variables in which the nonmetallic material can be treated mathematically as an infinitely thick solid (even though it might be of the order of several millimeters thick). This solution can be applied at short exposure times. The requirement of using material from the same base-stock as the actual vessel or lining has led to certain constraints because of size and thickness that have to be considered in setting up the experiment. Though in some instances more than one component might be diffusing into the nonmetallic, the assumption has been that the estimated diffusion coefficient is like an effective diffusion coefficient of the absorbing components. Following is a brief review of some procedures used to make these estimates. These procedures are the focus of this paper.

Tikhomirova et al.[5,6] and Borisov[7] attempted to estimate the diffusion coefficient in plastics by weighing immersed samples periodically and by plotting the logarithm of the mass gain as a function of time. The values guessed for the infinite time or equilibrium concentration were varied until the plot became a straight line that fit the data in a visually pleasing manner. The diffusion coefficient was evaluated from the slope of the line. The experimental times were short, the order of four days or less. This use of semilogarithmic paper assumes that only the first exponential term of the infinite expansion of exponentials dominates the solution. Justification of this assumption was not presented.

This approach was refined by Fisher and Carpenter[8,9] to eliminate the above need for deducing the diffusion coefficient from a hand-drawn plot. They used a computer program to try to fit the mass change with time to the analytical solution to the diffusion equation, again using only the first of the exponential terms of the series expansion. Their experimental procedure included an additional desorption step in an oven held at the same temperature as the absorption step to determine if desorption of components (e.g., plasticizer) from the nonmetallic occurred while the environment was absorbing into the nonmetallic. They concluded that Fick's law for one component could only be used for the absorption phase to model the mass change when there was no (or little) simultaneous desorption during that cycle. Otherwise, the mass change reflects more than one diffusion process and requires a second diffusion equation for a complete solution (assuming both processes are decoupled). This point tended to be overlooked by previous workers. Again, no justification was presented on the simplification of using the first of the exponential terms only for the experimental conditions described.

Jason and Peters[10] have successfully estimated diffusion coefficients involved in a bimodal diffusion process through fish membranes. They showed that for their particular situation, they could estimate two distinct diffusion coefficients by appropriate manipulation of the analytical solution to the diffusion equation. Thus, decoupling of diffusion processes to estimate two distinct diffusion coefficients from mass change information may be possible.

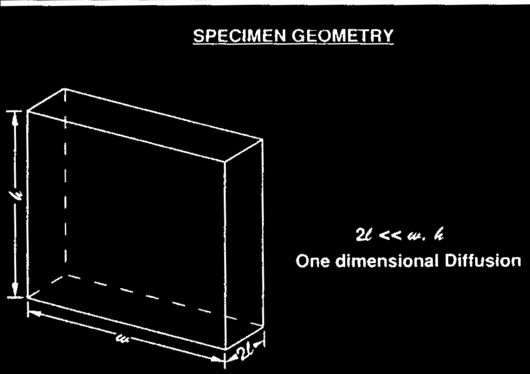
There is a major assumption in these approaches. The assumption is that the series solution to the diffusion equation converges rapidly enough so that the first exponential term becomes dominant and the sum of the balance of the terms become negligible. The applicable geometry and series expansion solution[3] for the experiments used in the above studies is shown in Figure 1. This solution is derived from the one-dimensional form of Fick's second law written as

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

The solution shown in Figure 1 is rewritten in Equation (2) to separate the first exponential term from the balance of the expansion for the discussions to follow. The equation becomes

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} e^{-\left[\left(\frac{Dt}{l^2}\right)\left(\frac{\pi^2}{4}\right)\right]} - \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n+1)^2} e^{-\left[\left(\frac{Dt}{l^2}\right)\left(\frac{\pi^2(2n+1)^2}{4}\right)\right]} \tag{2}$$

As shown in Equation (2), the variable that determines the magnitude of the exponential such that the terms within the summation



ANALYTICAL SOLUTION

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(-\left(\frac{Dt}{l^2}\right)\frac{(2n+1)^2\pi^2}{4}\right)$$

Obtain D, M_∞ from values of mass (M_t) vs time (t)

FIGURE 1. *Specimen geometry and analytical solution for estimating sorption properties.*

are negligible is the term diffusion coefficient times time divided by the square of the half-thickness, a dimensionless variable, Dt/l^2. Its physical significance is that it is the ratio of the actual time to the time for the penetrating molecule to move to the surface of a sphere whose radius is the half-thickness l, a measure of the time to move a distance l. This dimensionless group must be examined closely to determine the rate of convergence of the infinite series. For example, for diffusion coefficients of the order of 10^{-10} to 10^{-9} cm/s (predicted for diffusion of some liquids through rubber linings[8,9]), long times might be required for the first term to dominate so that the others can be ignored and still obtain a reasonably accurate estimate of the diffusion coefficient and concentration of absorbate at infinite time. That the use of the first exponential term only may not adequately determine the value of the series summation has not been demonstrated. The relationship among diffusion coefficient, test duration, and sample thickness to minimize this error resulting from neglecting all terms after the first needs to be determined.

A second approach to making these estimates is to monitor the amount of absorption for "short" times and then to plot the total absorption versus the square root of time. The diffusion coefficient is deduced from the slope of the straight line. This approach makes use of Equation (3)

$$\frac{M_t}{M_\infty} = \left(\frac{2}{\pi^{1/2}}\right)\left(\frac{Dt}{l^2}\right)^{1/2} \qquad (3)$$

which is the truncated solution to the diffusion equation after implementing the Boltzmann transformation. The summation of terms in the complete solution[3] involving the complementary error function are assumed to be negligible. The mathematics leading to this solution is discussed elsewhere.[3]

This transformation combines the variables of time and distance into one variable of distance divided by twice the square root of time. This method is often used to predict diffusion after short exposures because one of the boundary conditions is that the absorbate concentration approaches its initial condition as the transformed variable, $x/2t^{1/2}$, becomes infinite.[3] The application to short times arises from the observation that as time approaches zero, the transformed variable becomes infinite and the concentration approaches its initial condition.

This method has been used by Angus and Marshall[11] to estimate diffusion in pipe linings and by Southern[12] to estimate diffusion of water through rubber materials, among others. The results presented suggest that under certain conditions, the use of Equation (3) is valid. The question is what limitations are imposed on the experimental parameters by using Equation (3).

A third approach is to estimate the diffusion coefficient and the uptake at infinite time by using all of the contributing terms in Equation (2). Nonlinear regression is used. This approach has not been reported previously for engineering evaluations of nonmetallic materials.

This paper has several goals. The paper first examines how the requirements for using the methods discussed above create certain experimental restrictions. That is, the estimation procedure used affects the ability to estimate the diffusion coefficient for a given thickness and experimental test time. The paper then attempts to arrive at the best mathematical alternative for making this estimate. Three procedures are examined: (1) regression of the mass change against time using the complete analytical solution, (2) regression of the mass change against time using only the first exponential term, and (3) the solution assuming diffusion into a semi-infinite solid. The focus is on absorption in the absence of simultaneous desorption and so is restricted to a fairly simple case. However, the results should provide insight as to how these parameters might interact in more complex situations.

REGRESSION USING ALL TERMS

The geometry assumed for the analysis is shown in Figure 1. This geometry is typical of the specimens used in the studies reported to date. Included is the equation that determines the uptake as a function of time, thickness, and diffusion coefficient for that geometry. The slab is assumed to have a thickness that is much less than the width and height. Use of this geometry means that the diffusion process is one dimensional. This conclusion is best seen by noting that the concentration gradient, of the order of ΔC/distance, is much larger in the direction parallel to the thinnest direction, the thickness $2l$. Experimentally, this requirement can be achieved by using a thin sample, e.g., several millimeters. If this dimension is about an order of magnitude smaller than the other dimensions, then one dimensional diffusion can be assumed.

When constructing an experiment, one must know the actual magnitude of the thickness so that a physical sample can be prepared. Since the dimensionless variable is Dt/l^2, the required thickness should be related to the diffusion coefficient and the test duration. Small values of Dt/l^2 mean that the diffusing species has not penetrated far into the specimen. This term is important mathematically because it governs how the change in concentration gradient relates to the rate of uptake. This change in gradient is one parameter that may affect the ease with which a regression analysis can solve Equation (1) for the diffusion coefficient and uptake at infinite time. For example, a small gradient change may mean that small changes in the variables as imposed during the regression analysis have little effect on the objective function being minimized. This lack of sensitivity would mean that a large number of iterations might be required to minimize the objective function.

Use of the complete summation in Equation (2) to estimate the diffusion coefficient and M_∞ from M_t versus time data by regression using all terms was investigated in the following manner. Values were selected for D/l^2 and M_∞. These values are referred to as the "true values." Then a maximum value of time (the test duration) was chosen and this time was broken into 30 equal increments. A value of M_t was calculated at each time increment. These calculated values of M_t versus time represent the data for the regression analysis. The regression attempted to find the true values of D/l^2 and M_∞ from this mass versus time profile by starting with values of D/l^2 and M_∞ that differed from the true values by 0.1 and 10 percent.

Two regression routines were used. The first routine used most extensively is based on Marquardt's method. The algorithm itself has a long history of success on a wide variety of problems including the circuit analogue analyses of electrochemical impedance spectra.[13] It minimizes the sum of the squares of residuals between a calculated and actual objective function. An earlier version of the routine (called BSOLVE) has been published.[14] The second routine is based on the method of Nelder and Mead.[15] This routine seeks to minimize the function of a number of variables by comparing the function at the vertices of a general simplex. This procedure does not require derivative evaluations. In both cases, terms in the infinite series that were smaller than 1×10^{-16} were assumed to be equal to zero.

The ability of the regression analysis to calculate the specified diffusion coefficient and absorption at infinite time as a function of time was estimated by following how the routine proceeded in minimizing the sum of the squares of the residuals. A distinct boundary was found to exist in D/l^2 versus time space between regions in which the true solution could and could not be estimated by the regression analyses. Figure 2 shows a typical plot. The points that demarcate the boundary fall on a straight line when plotted in log–log format.

Figure 2 shows that the boundary is somewhat dependent on starting point and the algorithm used to perform the regression analysis. However, the boundary does not disappear. A boundary is found, but at a slightly different location that depends on the error in the starting point. Though only two algorithms and a small number of initial conditions were attempted, such a boundary between "Solution Unobtainable" and "Solution Obtainable" regions is believed to be a universal numerical phenomenon when using this approach. The reason is that the sum of the squares of residuals surface is flat with respect to small changes in the regressed variables. As experiment duration (time) is decreased, this insensitivity prevents the minimum in the objective function from being located. The time below which no solution is found is a function of the diffusion time, l^2/D, used in its inverse form in Figure 2. The minimum value of the exposure duration, t_{min}, for a given diffusion coefficient and thickness is given approximately by the relationship $Dt_{min}/l^2 > 0.17$. The existence of the boundary was verified by observing the slow change in the sum of the squares of the residuals with iteration in the region of the boundary. The number of iterations required to reach the minimum increased dramatically as the boundaries shown on Figure 2 were approached.

That the regression analysis might be used to estimate diffusion coefficients and mass uptakes at infinite time in the region marked "Solution Obtainable" was demonstrated in two ways. A sample of a thermoplastic elastomer (TPE) was immersed in deionized water at 95°C. Duplicate tests were run. The mass versus time profile was determined by periodically removing the samples, wiping them, weighing them, and then reimmersing them for the next time period. The absorption test lasted 45 days. A drying test run at the end of the absorption test in an oven at the same temperature showed that the mass returned to its original value, suggesting that no simultaneous desorption had occurred during the exposure to water. Thus assumption of diffusion of one component is reasonable. The mass versus time profiles of the two samples are shown in Figure 3. The results in D/l^2 versus time space are shown in Figure 2. Note that the profiles shown in Figure 3 result in the same estimated diffusion coefficient, but in slightly different equilibrium mass uptakes. This difference is most likely a result of the errors introduced during weighing and in measurement of thickness.

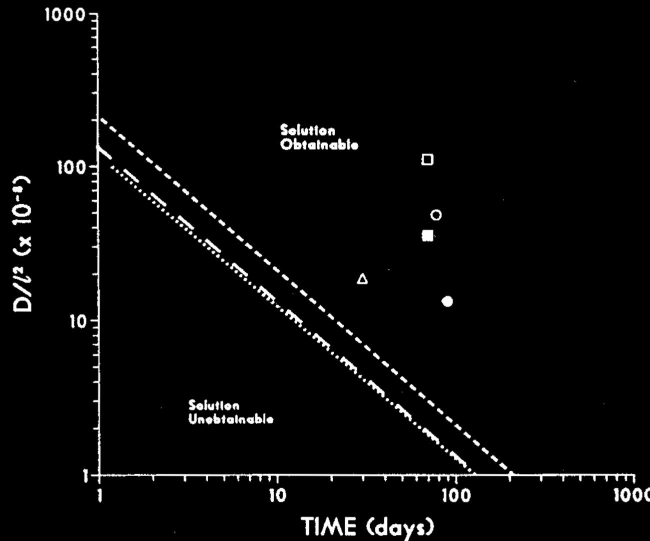


FIGURE 2. *Boundary between regions of solution and no solution. Included are results for Marshall (Reference 15) and TPE (Figure 3). Mass gain time at infinite time = 10%. Assumed error in diffusion coefficient = 10%. Data source: (— — —) 0.1%—regression 1; (- - -) 10%—regression 1; (····) 10%—regression 2; (●) fluoro-A; (○) fluoro-B; (□) nitrile; (■) laminate; (Δ) TPE.*

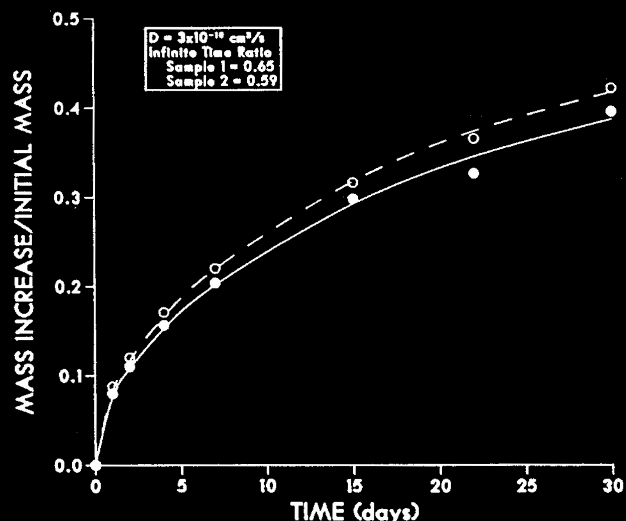


FIGURE 3. *Thermoplastic elastomer in deionized water at 95°C. Duplicate samples run. D = 3 × 10⁻¹⁰ cm²/s. Infinite time ratio: sample 1 = 0.65; sample 2 = 0.59.*
Sample 1 data: (●) measured, (——) calculated.
Sample 2 data: (○) measured, (– – –) calculated.

In addition, J.M. Marshall provided the original mass versus time data[16] used for the paper referred to previously.[11] The uptake versus time curves were used to estimate diffusion coefficients and infinite time concentrations. Regression analysis was successful in all of these cases. The results are included in Figure 2.

As can be seen, all results lie in the "Solution Obtainable" region of this figure. Unfortunately, there is not corroborating evidence for the accuracy of the diffusion coefficients and infinite time concentrations. Therefore, the absolute values may be in error. However, the important point is that Equation (2) can be used to estimate these parameters, but with the observations that the experiment must be designed so that the regression analysis can succeed and that some error might be introduced by the periodic removal of the sample for weighing and its reinsertion in the solution.

The practical implication is shown in Figure 4. The boundary in Figure 2 was used to create a new boundary as a function of test time plotted in the coordinates of diffusion coefficient and thickness. Three boundaries are shown that correspond to test durations of 3, 30, and 300 days. The boundaries correspond to 10 percent error in the initial guess and a 10 percent change in mass at infinite time. Included is the thermoplastic elastomer data point from Figure 2, which corresponds to a test duration of 45 days. The "Solution Obtainable" region lies below (to the right of) each line. The data point lies in this region, e.g., to the right of the 30-day line. Curves such as these, or the relationship $Dt_{min}/l^2 > 0.17$, can be used to estimate the required test time if the thickness is known and the diffusion coefficient is estimated or the required sample thickness estimated if the test duration is known and the diffusion coefficient is estimated.

REGRESSION USING FIRST EXPONENTIAL TERM ONLY

A more popular method that has been used to estimate the diffusion coefficient and infinite time concentration has been to fit the first two terms of Equation (2) to a mass change profile.[5–9] This approach makes the implicit assumption that the terms for n greater than zero in the summation are negligible. Examination of Equation (1) suggests that the variable Dt/l^2 should be important in determining the validity of the assumption. The size of each term depends on the value of e raised to the negative of this variable. Thus, time, thickness, and diffusion coefficient do not individually determine the validity of the assumption of relative size of terms.

The assessment of using only the first two terms of Equation (2) for making an estimate of M_∞ and D was made using Equation (4),

$$1-\left(\frac{8}{\pi^2}\right)e^{-\left[\left(\frac{Dt}{l^2}\right)_{calc}\left(\frac{\pi^2}{4}\right)\right]} = 1-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}e^{-\left[\left(\frac{Dt}{l^2}\right)_{true}\left(\frac{(2n+1)^2\pi^2}{4}\right)\right]} \qquad (4)$$

For various values of $(Dt/l^2)_{true}$, corresponding values were estimated for $(Dt/l^2)_{calc}$ such that Equation (4) is fulfilled. Figure 5 shows the comparison of the two dimensionless groups.

Significant deviation of the values occurs at true Dt/l^2 values as large as 0.2. A 10 percent error will arise at true Dt/l^2 values of about 0.08. The important point is that using the shortened analytical solution results in an asymptote for Dt/l^2. No positive value of $(Dt/l^2)_{calc}$ can be found for values of $(Dt/l^2)_{true}$ less than about 0.03. This finding implies that for short times, e.g., the one week sometimes used,[5–7] and thicknesses of several millimeters, e.g., 3 mm, the minimum diffusion coefficient estimable with a 10 percent error in the dimensionless group is about 3×10^{-8} cm/s. For these conditions, diffusion coefficients of less than 5×10^{-9} cm²/s lie in the region to the left of the asymptote. Diffusion coefficients of this magnitude cannot be calculated by using only the first two terms in Equation (4).

Usable rubber and plastic types of materials often require diffusion coefficients of less than 10^{-9} cm²/s or so to be reasonable barrier materials.[9] For example, rubber materials have been predicted to have diffusion coefficents for water at room temperature of the order of 1 to 5×10^{-10} cm²/s.[8] Use of only the first exponential term of the analytical solution may require longer test times or thinner samples than if the full solution were used for the regression analysis. Values of Dt/l^2 smaller than about 0.25 cannot be calculated by this procedure. If either the time or thickness is chosen improperly, diffusion coefficients could be grossly overestimated by this analysis. The result would be that potentially acceptable materials might be rejected.

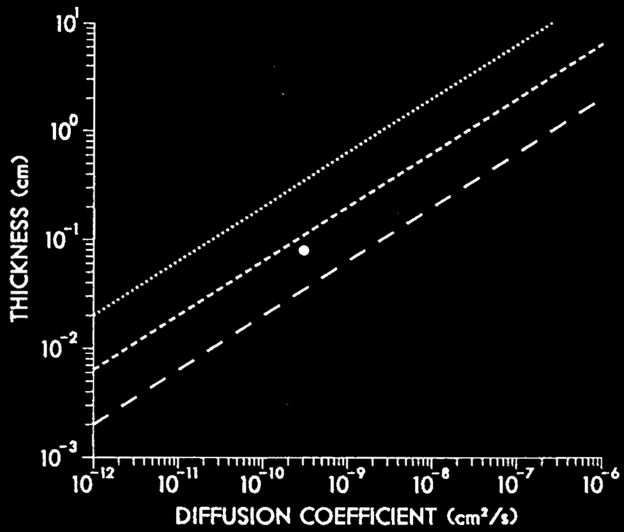


FIGURE 4. *Maximum sample thickness vs diffusion coefficient for various times of exposure for the regression analysis of the full analytical solution to be successful. Included are the diffusion coefficient, exposure time, and thickness data from Figure 3. Test time: (— — —) 3 days; (- - -) 30 days; (····) 300 days. (●) TPE.*

In addition, even if the total test time is appropriate, the first two terms of the summation might not adequately represent the mass versus time profile for the first few measurements made early in the exposure. The regression analysis would be incorrect for those data points. This statement would be true for those points for which $(Dt/l^2)_{true}$ is less than about 0.03. This situation would not be uncommon when evaluating materials with practical diffusion coefficients.

The required test time to make the "True" and "Calculated" values of Dt/l^2 in Figure 5 be within 10 percent of each other can be estimated as a function of diffusion coefficient and thickness. This 10 percent value is used for the sake of argument. Similar figures could be developed for other values. Figure 6 shows this estimate. Included are some of the results estimated by previous workers.[5–9] The valid region that causes less than a 10 percent error in the dimensionless group lies below (to the right of) each line. Test times of 3, 30, and 300 days are shown.

Tikhomirova et al.[5,6] and Borisov[7] tended to perform their experiments for five days or less. Their data when plotted on Figure 6 show that the results for absorption of nitric acid by polytetrafluoroethylene (PTFE) are probably inaccurate, especially those results that suggest a diffusion coeffient of 10^{-9} cm²/s or less. The others may be reasonable. Fisher and Carpenter tended to run their tests for 30 to 100 days depending on the material. As shown, their test duration should place their results in the region of the curve in Figure 5 in which the true and calculated values of Dt/l^2 are similar.

The small diffusion coefficients estimated in some of the reported tests suggest that the use of only the first exponential term in the solution is not an improvement in the analysis procedure. Estimating small diffusion coefficients with samples of reasonable thickness (e.g., several millimeters) would require test times of 50 to 100 days to minimize the error in the estimated dimensionless group (and a complementary error in the absorption at infinite time). Use of one exponential term in place of the complete analytical solution does not make the data analysis and test simpler or more efficient. Indeed, some of the results reported in the literature as discussed previously using this approach are in error because of inadequate experimental design or inappropriate estimation procedures.

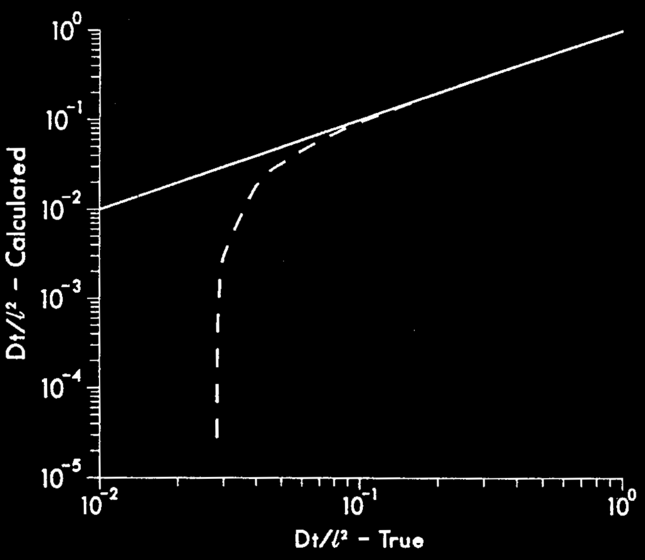


FIGURE 5. *Dt/l^2 as calculated from first term as a function of the true Dt/l^2. The difference is the error caused by including only through the first exponential term in the analytical solution.*
Solution used: (——) full solution, (– – –) first term only.

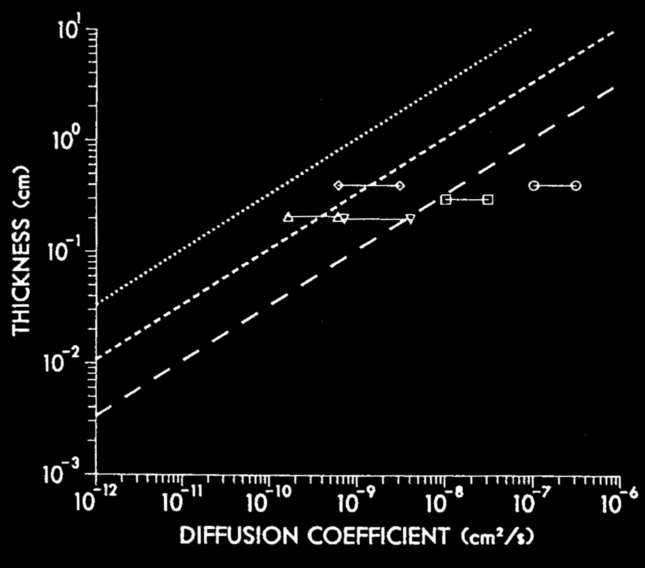


FIGURE 6. *Maximum sample thickness vs diffusion coefficient for various times of exposure for the diffusion coefficient estimated by including only through the first exponential term to equal the true diffusion coefficient. Test time: (— — —) 3 days; (- - -) 30 days; (····) 300 days. (◇) Tik – PTFE/nitric; (○) Tik – PE/PIB-nitric; (□) Borisov; (Δ) Carp – rubber/water; (∇) Carp – rubber/HCl.*

ESTIMATION USING BOLTZMANN TRANSFORMATION

The last procedure is to use the solution resulting from substituting the Boltzmann transformation in Equation (1). This solution is derived by performing a change in variables so that the time and thickness become a new variable in which the thickness is divided by the square root of time. This transformation changes the partial differential equation to an ordinary differential equation with the important boundary condition that as the distance divided by the square root of time approach infinity, the concentration approaches zero. This solution is valid for thick solids ($l \rightarrow \infty$) or for short times ($t \rightarrow 0$). The solution is in terms of a complementary error function, which for short times is given by Equation (3) above.

This equation has been used by a number of workers to estimate diffusion coefficients.[10,11,16] The reason is as follows. Figure 7 shows a plot of the slope of the mass uptake curve defined by Equation (1) versus the parameter $(Dt/l^2)^{1/2}$. This curve was obtained from the analytical first derivative of Equation (1) as a function of this dimensionless parameter. Included is the constant $2/\pi^{1/2}$. Significant deviation occurs between the slope of Equation (2) with respect to $(Dt/l^2)^{1/2}$ and the slope from the Boltzmann solution at a Dt/l^2 of about 0.25. Assuming that the dimensionless group must be less than this value for the Boltzmann transformation to be valid for the physical situation and that the thickness of the sample is 0.3 cm, diffusion coefficients of 10^{-10}, 10^{-9}, and 10^{-8} cm^2/s could, in principle, be determined from experiments that last for up to about 2×10^8, 2×10^7, and 2×10^6 seconds (about 200, 20, and 2 days, respectively). Thus, small diffusion coefficients could, in principle, be estimated by using this approach.

However, there are two drawbacks to using this method. The first drawback is that M_∞ cannot be separated from D in the slope. The reason is that there are two unknowns (D and M_∞) and one term to define them, the slope. Therefore, the uptake at infinite time would still have to determined from a separate experiment or by allowing the absorption to continue until equilibrium is achieved. In the case of large diffusion coefficients (e.g., 10^{-8} cm^2/s), this equilibrium is achieved fairly rapidly.[16,17] However, nonmetallics of practical interest usually have much smaller diffusion coefficients. Waiting for equilibrium is usually not practical so a separate experiment would often have to be run to estimate the uptake at infinite time. Since both parameters can be estimated by using the other two methods, there is no advantage in designing an experiment to use the mathematical simplification offered by the Boltzmann transformation.

The second drawback is the fact that the slope of the experimentally determined mass uptake versus square root of time curve is being used to obtain the diffusion coefficient. To determine a slope accurately from experimental data requires fairly accurate data with a minimum of scatter. Obtaining the mass change profile from weighings will place some error in the results, especially at short times when two relatively large numbers are being subtracted to obtain a relatively small number. Angus and Marshall attempted to circumvent this problem by using a radioisotope technique.[11] However, their data was still prone to a fair amount of scatter at short times. They still had to perform a second experiment to obtain the mass uptake at infinite time. Since the previous two analysis techniques both use the actual profile and not the slope, they would be more tolerant of errors in the mass measurement.

CONCLUSIONS

▶ Regression of the mass versus time profile against the complete analytical solution to the diffusion equation is a reasonable approach to estimating and predicting diffusion and sorption when Fickian behavior applies.

▶ Use of only the first of the exponential terms in the infinite sum offers no advantage to using all terms for estimating diffusion and sorption. Indeed, this approach places additional restrictions on the experimental design.

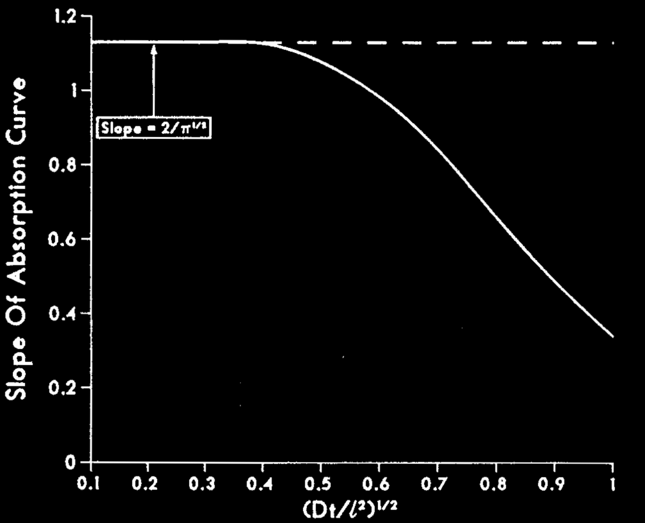


FIGURE 7. *Slope of the absorption curve (M_t/M_∞) from the full analytical solution and the Boltzmann transformation as a function of ($Dt/l^2)^{1/2}$. Slope source: (——) actual derivative, (- - -) Boltzmann.*

▶ The solution resulting from the Boltzmann transformation of variables does not separate the diffusion coefficient from the absorption at infinite time. An additional experiment is required to estimate the equilibrium uptake.

▶ The dimensionless group Dt/l^2 must be considered when choosing the test time and sample thickness. Otherwise, results can be in significant error.

▶ Presently reported results using above methods (2) and (3) may be in error.

▶ The guidelines provided refer only to absorption in the absence of desorption. Further work is required to extend these analyses to the case of simultaneous absorption and desorption.

REFERENCES

1. Process Industries Corrosion ed. B.J. Moniz and W.J. Pollock (Houston, TX: NACE, 1986), p. 573 to 639.
2. ASTM Standard D471-79, "Rubber Property—Effect of Liquids," vol. 09.01, ASTM Annual Book of Standards (Philadelphia, PA: American Society for Testing and Materials [ASTM], 1989.
3. J. Crank, The Mathematics of Diffusion (Oxford, UK: Oxford University Press, 1975).
4. P.E. Cassidy, T.M. Aminabhavi, and C.M. Thompson, Rubber Chem. and Technol. 56, 3(1983): p. 594.
5. N.S. Tikhomirova, K.I. Zernova, and V.N. Kotrelev, Soviet Plastics, no. 12, (1962): p. 36.
6. N.S. Tikhomirova and V.N. Kotrelev, Soviet Plastics, no. 10(1964): p. 38.
7. B. I. Borisov, Soviet Plastics, no. 4(1964): p. 50.
8. C.N. Carpenter and A.O. Fisher, Materials Performance 20, 1(1981): p. 40.
9. A.O. Fisher and C.N. Carpenter, "Elastomeric Linings," in Press Industries Corrosion, ed. B.J. Moniz and W.I. Pollock (Houston, TX: NACE, 1986), p. 589.
10. A.C. Jason and G.R. Peters, J. Phys. D. 6(1973): p. 512.
11. A. Angus and J.M. Marshall "The Effect of Crude Oil on Pipe Lining Materials," presented as paper no. 13 at International Conference Diffusion in Polymers, Mechanisms and Applications, City Conference Center, London, England, January 8–9, 1986.
12. E. Southern, "Diffusion of Liquids Through Rubbers," in Proceedings of the Conference on Rubber in Offshore Engineering (London, UK: 1983), p. 262.
13. D.C. Silverman and J.E. Carrico, Corrosion 44, 5(1988): p. 280.
14. E.J. Henley and E.M. Rosen, Material and Energy Balance Computations (New York, NY: John Wiley and Sons, 1969), p. 560.
15. J.M. Marshall, personal communication, 1988.
16. I.P. Eyerer and Th. Wurster, Adv. Polymer Technol. 4, 2(1984): p. 155.
17. A.R. Birens, J. Amer. Water Works 77(1985): p. 57.

APPENDIX A

List of Symbols

C	=	concentration (mol·cm^{-3}) of species at time t and distance s
D	=	diffusion coefficient (cm^2·s^{-1})
l	=	sample half-thickness (cm) (sample thickness = $2l$)
M_∞	=	mass uptake (g) at infinite time by nonmetallic
M_t	=	mass uptake (g) at time t
t	=	time (s)
x	=	distance (cm) into specimen (one-dimensional diffusion)