In Defense of the Diffusion Equation

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Abstract

The diffusion equation is shown by examples to properly account for absorption, desorption, and permeation phenomena in polymers when solved with suitable boundary conditions and concentration dependent diffusion coefficients. Stress relaxation, mechanical, or related explanations are not required. For absorption a surface condition allowing a slowly increasing surface concentration has been almost universally neglected in the literature. This has led to a variety of proposed theories to explain the absence of linear absorption on a square root of time plot. A boundary condition utilizing a significant surface mass transfer coefficient is shown to explain "anomalous" behavior. The presumed step-like advancing front of methanol absorbing into a sheet of PMMA at 30°C that is generally considered characteristic of Case II absorption is not found. The iodine tracer used in this system by Thomas and Windle was not suitable for the purpose of following methanol, lagging it considerably. Super Case II experiments are also readily modeled. The surface mass transfer coefficient reflects external factors such as diffusion in the external media near the polymer surface, diffusion in a stagnant boundary layer at the surface, condensation/evaporation steps, and the heat transfer necessary to keep the temperature of the film reasonably constant. A more subtle and much lower surface mass transfer coefficient can result from difficulties encountered in superficially adsorbed molecules passing through the surface. The molecules must orient correctly at suitable points of entry that are large enough before this can be achieved. In addition to size and shape factors, this orientation and entry is more difficult with poor solvents since these are not readily accepted by the polymer, and their molecules may be forced to orient adversely to the optimum positions that yield the easiest entry.

1. Introduction

Diffusion in polymers is a very important aspect of performance in many situations, particularly where barriers are required, for example in food and medical packaging, chemical protective gloves, and protective coatings of various kinds. The diffusion equation can model diffusion in polymers including absorption, desorption, and permeation, as is shown in the following, but there is a little more to barrier properties than diffusion alone. Solubility in the barrier polymer determines the overall concentration gradient that is the driving force for the diffusion process.

The (Hansen) solubility parameters (HSP) for the chemical and for the polymer must be sufficiently similar for it to be in the polymer in the first place [1-3]. This immediately gives a strong indication that the best barrier polymers have HSP as different as possible from the HSP of the chemical involved to reduce its equilibrium solubility as much as possible. Additional support for this is given in the following. Given some solubility of the chemical in the polymer one can analyze how quickly it will move under different circumstances and potentially optimize given situations for barrier materials. The analyses presented here are based on early experience with comparatively slow computer modeling [1,4] supplemented by more recent expansion of modeling capacity with the personal computers that now allow relevant solutions to be found rapidly for the all-important diffusion equation (Fick's Second Law) [3]. The same modeling methodology has been shown to duplicate experimental behavior for permeation through chemical protective gloves [3], to provide a consistent explanation for absorption in polymers in various experiments where the absorption does not follow a straight line on a square root of time plot [5], and to model film formation by solvent evaporation (desorption, solvent retention) [1, 5,6]. A significant surface condition has been necessary to do this. The earlier studies have now been extended to include modeling of key experiments in the literature typical of sigmoidal (S-shaped), Case II, and Super Case II absorption. A significant surface condition is required to fully explain such experiments. An attempt has been made to demonstrate the general usefulness of the diffusion equation supplemented by the insights that HSP can provide. HSP are available or can be measured or estimated for gases, liquids, pharmaceuticals, and polymers [2,3]. This allows comparison of the HSP for a very large number of chemicals and film barrier types.

2. The diffusion equation

The diffusion equation has a very general derivation based on the simple logic that what comes in must either go out or be accumulated. For a given time interval, the accumulation may be positive if a local element gains material or negative if there is a loss. Because analytical solutions to the diffusion equation are limited in scope, the results presented here are all based on numerical solutions. The discussion is simplified by considering mass transport in one direction only. Fick's First Law, given in Eq. 1, is used to derive the diffusion equation (Fick's Second Law given in Eq. 3). Eq. 1 gives what comes in on one side of a local region and what goes out on the other side.

Fick's First Law, is given here for mass transport in one direction only:

$$F = -D(c)dc/dx \tag{1}$$

This equation states that the flux at the given point, F, in the preferred units $gcm^{-2}s^{-1}$, is equal to the diffusion coefficient, D(c), in preferred units cm^2s^{-1}, times the concentration gradient, dc/dx. c is the concentration in preferred units gcm^{-3} with the distance x being given in cm. The negative sign is because the transport is in the direction of increasing x. The concentrations and calculations here are based on the dry polymer with the film being divided into intervals (grid in

the figures). The diffusion coefficient is expressed as $D(c)$ since it depends on concentration as shown at the upper right in the figures that follow. The reason for this dependence on concentration is that the free volume of the system increases with the addition of smaller molecular species. This allows for more rapid polymer chain segment motion. The polymer chains block the motion of the diffusing species and when they can move more easily, the movement of smaller species is also facilitated.

It is very important to note that not only is Eq. (1) valid for the bulk of the polymer, but it is also valid for the relevant surfaces as given in Eq. 2. This equation is given prior to the diffusion equation since it is at the heart of this whole study. As shown in the following it is a necessary boundary condition to model most of the examples in the following.

$$F_s = h(c_e - c_s) = -D(c)dc_s/dx \qquad (2)$$

For absorption this equation says that the mass passing through the surface that comes from the exterior, F_s, is equal to the mass transferred through the surface into the bulk. In Eq. (2) the subscript s indicates surface values and h is a surface mass transfer coefficient with preferred units of cms^{-1}. c_e is the final surface concentration in absorption. This is most often equal to the amount that the polymer can absorb at equilibrium with liquid contact, for example, but can also be the amount taken up at equilibrium for an experiment at some partial pressure of vapors. The mass transfer coefficient will be discussed in more detail below. It may appear that mass transfer would stop when c_e is or becomes equal to c_s. In fact c_s will never quite reach c_e until the film is completely filled to the same concentration, in which case mass transfer does stop. In several of the examples below the mass transfer does progressively slow down for this reason as the film approaches the final state in an asymptotic manner.

The diffusion equation, Eq. (3), is usually solved with mass transport in one direction only in a plane film. This is done for the sake of simplicity and to enable more direct interpretation of experimental results:

$$dc/dt = d(D(c)dc/dx)/dx \qquad (3)$$

An elegant derivation of the diffusion equation is given starting on page 2 in Crank's monumental work *The Mathematics of Diffusion*. This work is cited several times in the following not out of respect for its age, but because it contains information and data that are just as timely today as they were over 50 years ago.

Solutions to the diffusion equation require an initial condition and two boundary conditions. The initial condition is usually taken as zero concentration throughout the film for absorption and permeation experiments. In the modeling done with the software available from [3] that is used here, one can follow how the film fills with time for absorption or reaches a breakthrough to the unexposed side in permeation modeling. This is given at the lower left in the figures below. An initial uniform concentration in the film is assumed for desorption, and one can follow how the

depletion proceeds with time. The concentration gradients can also be meaningful, showing the dominance of the surface condition when they are horizontal, for example. Concentrations are normalized for the sake of generality with 1.0 being the highest concentration encountered and 0 being the lowest.

For absorption the surface concentration is almost universally (and frequently erroneously as will be shown below) taken as the final value from the very start. In this report what happens at the exposed surface in absorption is dictated by the boundary condition given in Eq. (2). If the surface mass transfer coefficient is high enough, the surface concentration will indeed effectively rise to the final value immediately. If h is low enough to be significant, the surface concentration will rise as some rate determined by its value relative to the diffusion coefficients as determined by the diffusion equation. The increase of the surface concentration with time is frequently exponential since this reflects absorption controlled by the surface condition. The surface concentration as well as any local concentration within the film can be read at all times from the screen in the software used here. It will be shown in the following that h can be so low as to completely dominate an absorption experiment. The almost universal neglect of a significant surface condition has led to many explanations for absorption phenomena that do not plot as a linear uptake with the square root of time. Some of these are discussed below.

The second boundary condition describes what happens at an impermeable substrate or in the middle of a free film with exposure on both sides. There is no mass transport in the middle of such film or at an impermeable substrate, so F is zero in such cases. This means the concentration gradient is zero for such conditions according to Eq. (1). For permeation this second boundary condition describes what happens at the surface where the permeating chemical leaves the polymer film. The concentration here is usually assumed to be zero, but this may not always be the case if there is something preventing immediate loss from the film. Here again Eq. (2) may become significant, such as for a solvent with low volatility, or slow removal of the solvent from the external environment.

The diffusion coefficient is rarely a constant for solvents in polymers with this being valid strictly speaking only at concentrations approaching zero, D_0. A mathematical expression for how the diffusion coefficient behaves in polymers as a function of solvent concentration, $D(c)$, is required to properly solve the diffusion equation. $D(c)$ is normally an exponential function of the concentration of the diffusing species for polymers. Typical examples of $D(c)$ are given in the following examples. Only data within the range of concentrations being considered in a given example are used.

There are three regions that may require diffusion coefficient data. These are for a rigid polymer at lowest solvent concentrations, an intermediate solvent concentration region for otherwise rigid polymers or for a rubbery polymer or elastomer, and finally a viscous liquid region at low polymer concentrations. Diffusion coefficients in the rigid polymer have been measured to depend exponentially on the local concentration with correct accounting for this as shown for

example in [1,2,5,7]. Both absorption and desorption experiments, when interpreted in accordance with the diffusion equation, gave the same results. The diffusion coefficients in the intermediate region have also been found to be exponentially dependent on concentration by absorption experiments that required consideration of a significant boundary condition as well as concentration dependence [2,4,5]. The final region is more liquid-like, but the diffusion coefficients still vary with concentration but not as strongly as in the lower concentration regions. For the sake of convenience the exponential dependence has also been assumed here although this has not been experimentally confirmed. Diffusion at these low polymer concentrations is not considered in the following so any errors resulting from this assumption are minimal. The self diffusion coefficient for many liquids is close to $(10)^{-5}$ cm^{2}s^{-1}. This places an upper limit on what diffusion coefficients can be assumed when experimental data are lacking. It should be remembered that diffusion coefficients for common solvents in polymers can easily be $(10)^{-15}$ cm^{2}s^{-1}, or even lower, at close to zero concentrations. An immense range of diffusion coefficients must sometimes be dealt with for proper understanding, interpretation of experiments, and modeling. A major problem in the relevant literature is that this has not generally been done. The examples below frequently involve diffusion in the rigid as well as in the elastomeric regions of behavior in the same experiments. Such situations require numerical solutions for the diffusion equation.

3. Fickian Absorption

There have been many studies of absorption in polymers and many theories of why the absorption curves sometimes are not "Fickian", that is not straight lines using a square root of time plot. Vesely describes these theories and some of their advantages and shortcomings in a comprehensive review [8]. Several examples are given in the following to illustrate that the diffusion equation can account for the different "anomalies" observed in key studies the literature. In all cases the initial condition for absorption is for a completely dry film.

The first example is for reference to demonstrate what is conventionally called "Fickian" diffusion for absorption using a constant diffusion coefficient equal to $1(10)^{-8}$ cm^{2}s^{-1} and a free film that is 0.2 mm thick. The settings are such that a realistic comparison with diffusion of solvent in a polymer can be done in the second example, otherwise this would not be included since Crank [9], among others, has published corresponding results. The surface concentration is taken as 0.2 volume fraction. This is a fictitious example since any absorption to that amount would drastically change the diffusion coefficients.

The surface concentration does not enter into or affect the calculations on a relative basis when the diffusion coefficient is a constant. The same result on a relative basis would be found for a surface concentration of 1%v as for 90%v. The required rate of mass transfer is much larger in the latter case since the time span for the experiment is the same. This kind of situation can lead to an unrecognized significant surface condition in practice since material can be transported by diffusion away from the surface into the bulk faster than it can arrive at the surface, condense,

and proceed with entry into the bulk. In such a situation the absorption curve would probably be sigmoidal or S-shaped of the type as shown in Fig. 3 below.

In the following examples it will be shown that the diffusion equation can also yield other types of uptake curves, but that all of these are in principle "Fickian" since they are readily modeled by solutions to the diffusion equation.

The next example is also fictitious, but in the opposite extreme. Fig. 2 shows that the absorption is linear on a plot of uptake versus the square root of time, even when the diffusion coefficient increases by a factor of $(10)^6$ over the concentration interval of interest. The diffusion coefficients at the upper right are carefully measured for chlorobenzene in poly(vinyl acetate) at 25°C in a series of extensive studies as mentioned above [1,2,5]. The concentration dependence at all concentrations was considered as was a significant h at concentrations above 0.2 volume fraction for absorption experiments. The linear absorption curve extends to nearly complete saturation, whereas for the constant diffusion coefficient case in Fig. 1, the absorption curve starts to flatten above about 60% equilibrium absorption. The concentration gradients approach what might be called an advancing front. It is clear that a more extreme change in the diffusion coefficients over the concentration range of interest is required before a step-like advancing front would be found unless other factors are involved.

4. 2-Step, S-shaped or sigmoidal absorption

The absorption of supercritical carbon dioxide into a 1 micron thick PMMA film on a quartz microbalance was measured and modeled by Carlà et al. in [10]. The amount absorbed is less than 1%v. The results were discussed in [10] using an approach based on relaxation of stresses in the polymer as a significant element in the analysis. This procedure has been called the NET-GP approach for non-equilibrium thermodynamics in glassy polymers with references in [10] giving the details. The results shown in Fig. 3 confirm that consideration of stress relaxation and related phenomena are not required to explain these experiments since the absorption curve is matched by these calculations using the diffusion equation and a very significant boundary condition.

The time to reach equilibrium is 20-30 minutes for the 1 micron films. The explanation provided in [10] involves bulk phenomena only. This means that the *effective* diffusion coefficients in the bulk that would be required to model the experiment, although not measured, estimated, or mentioned must be very low. This reduction is accomplished by the short-term bulk viscosity parameter, η^*, in the NET-GP approach. An estimate of the average *effective* (constant) diffusion coefficient in the bulk of the polymer can be found from solutions to the diffusion equation for a constant diffusion coefficient considering the time required to essentially saturate the film. The value found is near $5(10)^{-12}$ cm^{2}s^{-1} which is about 4 orders of magnitude lower than the expected diffusion coefficient(s) near $1(10)^{-7}$ cm^{2}s^{-1} or perhaps slightly lower. Such a low value would seem improbable. The major resistance to absorption is at the surface and would appear to be caused by problems of the carbon dioxide getting through the surface. With this interpretation

the expected diffusion coefficient(s) can be maintained. The value for h that accomplishes this is $2(10)^{-7}$ cms^{-1}. This is a reasonable value judging by the room temperature h values reported in Table 1, but it cannot be compared directly because of experimental conditions being 50°C and high pressure for a very small molecule. The surface concentrations in this modeling match those reported in the last figure of [1]. The studies in [10] are discussed in more detail in [11].

The absorption of water vapor into poly(vinyl alcohol) from a dry initial condition to very high final values that would yield viscous films is reported in [12]. An example from this study was analyzed in [5]. This experiment clearly shows the S-curvature at the start. The initial curvature is very dependent on the concentration dependent diffusion coefficients used for the modeling. The reasonable diffusion coefficients that were assumed showed that after about 0.1 volume fraction is absorbed, further absorption to an equilibrium value of 0.748 volume fraction of water is completely controlled by the surface condition. At concentrations higher than 0.1 volume fraction the diffusion within the film is much faster than water can get to or through the surface and the concentration profiles are horizontal throughout the film. The results were interpreted in terms of stress relaxation in [12]. If the process is reversed with desorption from this kind of viscous film with a high water content, one would naturally assume that the external factors of diffusion in the air, vapor pressure of the water, heat transfer to evaporate the water, etc. would be used to model the process. The results of a film drying study of this kind would be similar to those shown in Fig. 8.

Additional examples of sigmoidal absorption where h has been estimated are given in [13] for several liquids in contact with a COC polymer Topas® 6013 from Ticona. The data in Table 1 are taken from this source. It is noteworthy that the liquids that showed this two stage behavior were poor solvents. This is discussed in more detail below.

It should also be remembered that Crank [9] provided figures with two-stage absorption for the cases of an exponentially increasing surface concentration as well as for cases of different (significant) values of the surface mass transfer coefficient that he called α.

5. Case II absorption

Thomas and Windle studied the absorption of methanol into PMMA at several temperatures in a series of papers [14-20]. The absorption of methanol into PMMA at 30°C as reported by Thomas and Windle shows linear uptake on a plot using linear time. This result has been accepted universally as typical of what has been called Case II absorption. The exponential diffusion coefficients estimated at the upper right in Fig. 4 are in agreement with what is expected for a smaller molecular species in a rigid polymer. D_0 is modeled to be $5(10)^{-11}$ cm^{2}s^{-1}. Berens and Hopfenberg report D_0 for methanol in PMMA at 30°C [22]. This value $1.6(10)^{-11}$ cm^{2}s^{-1} compares well with the value used in Fig. 4. The agreement is presumed to be better than these numbers indicate when it is recognized that the diffusion coefficients included in [22] did not account for a significant surface condition. Had this been done the reported diffusion coefficient

would be higher since the added resistance to mass transport from the surface effects were ascribed to diffusion. Windle showed that when the rate of cooling through the glass transition temperature was 13.3 °Cs^{-1} there was a time lag on a square root of time plot equal to 1.2 hours. When the rate of cooling was 0.01°Cs^{-1} this was extended to 5 hours [20]. This confirms that rearrangement at the surface of the PMMA chain segments is still taking place when samples are simply removed from ovens. The diffusion coefficients assumed for the modeling are considered to be in satisfactory agreement with literature data in view of potential differences between practices and samples from different laboratories. Reasonable curve fitting was also possible by slightly adjusting several of the parameters with a forced D_0 equal to $3(10)^{-11}$ cm^{2}s^{-1}, but the general picture is not changed and the original attempt that appeared better is maintained.

The linear uptake curve at the lower right in Fig. 4 duplicates the straight line found in [14,17]. A significant surface mass transfer coefficient equal to $1.08(10)^{-6}$ cms^{-1} is required to do this. A theory as to why a significant surface mass transfer coefficient is found for this system is given in the discussion below. While it may be a coincidence, this h value would fit well into the data given in Table 1.

The results in Fig. 4 are very significant since the step-like, advancing front concentration gradients reported by Thomas and Windle for methanol in PMMA are not found. Case II absorption has otherwise been widely associated with concentration gradients that have an advancing front behavior based on these studies. The iodine tracer that was believed to follow the methanol accurately demonstrated a flat concentration profile with the iodine "fronts", given by the depth of penetration, finally meeting in the middle of the free film. Methanol is calculated to reach the center of the free film after about 9 hours. The Iodine tracer absorbs into the methanol swollen PMMA with flat profiles with "fronts" that meet in the center of the free film after about 23 hours. Since this is about the same time at which the film becomes saturated with methanol, the reliability of the iodine tracer method was accepted, and this implied a step-like advancing front for methanol. This simultaneous meeting of the iodine "fronts" with the completion of absorption of methanol was not found at higher temperatures, however. It should be clearly emphasized that step-like concentration gradients do not exist for methanol in this system according to the analysis presented here that is based on the diffusion equation alone. Quite to the contrary, the concentration gradients are horizontal rather than vertical above an absorbed amount equal to about one-half of the final value. There is a more detailed analysis of the absorption of iodine and methanol into methanol-swollen PMMA at different temperatures using data from these studies in [21]. It would appear unnecessary to have alternate explanations for the absorption of methanol into the PMMA based on the above analysis.

6. Super Case II absorption

The studies of Hopfenberg and coworkers [23-27] on diffusion in poly(styrene) also provide data for analysis by the diffusion equation. An often cited example from the literature where the

absorption curve shows an increasing absorption rate with linear time (Super Case II) is found in [23,24] as well as in [14]. This is modeled in Fig. 5.

The experimental data for the absorption of n-hexane into poly(styrene) reported originally in [23,24] and also found in [14] have been modeled successfully in Fig. 5. The surface condition dominates the absorption almost from the start as demonstrated by the flat concentration profiles. The sharp increase in the diffusion coefficients is unusual, but is required to produce the curvature in the absorption curve with the same experimental features. There are several reasons individually or collectively that could contribute to this. There is considerable retained solvent in the samples so there is a strong plasticizing effect already in place. There is apparently orientation in the samples used in this and other studies by the group [23-27], and the linear molecules of n-hexane can diffuse rapidly without the hindrance of side groups once they are in the film. The retained solvent is located uniformly within the interior of the film with a sharp drop in concentration to zero at the surfaces. Once a small amount of n-hexane gets through the surface skin, it will immediately meet a region where diffusion will be much more rapid. This effect cannot be modeled as such with the present software, but has forced the diffusion coefficients to be essentially those as given in Fig. 5 to model the experimental data. These cannot be taken as the true diffusion coefficients for n-hexane in polystyrene, and indeed the diffusion coefficients of solvents in any polymer will depend strongly on the prior history of the samples. The D_0 for n-pentane in polystyrene is given as about $3(10)^{-12}$ cm^{2}s^{-1} at this temperature in [23], compared with $1.3(10)^{-12}$ cm^{2}s^{-1} used here for n-hexane, so this estimate is reasonable considering the slightly larger molecule. The rate of uptake is reported in [24] for n-hexane into polystyrene at the conditions modeled here. The initial rate of absorption is $2.3(10)^{-4}$ mgh^{-1}cm^{-2}. Using the initial flux, F_0, and initial concentration difference at the surface, Δc_{s0}, in the approximate relation given in [2,4] for the surface mass transfer coefficient , $F_0 = h\Delta c_{s0}$, gives h equal to $7.5(10)^{-10}$ cms^{-1}. The h used in the modeling was $4.4(10)^{-10}$ cms^{-1}. This was required to end the absorption process at the right time. The h calculated here from the reported initial rate is probably higher because of an upward bias in the initial slope due to the first data point. This is clearly seen in the original data. Δcs_0 is the concentration difference using the final concentration minus zero in g$_{solvent}$cm^{-3} of dry polymer. This relation is reasonably accurate here since the surface condition is so dominant in this experiment. The agreement is surprisingly close, and further confirms the necessity to use Eq. 2 in the modeling. If one tries to use the calculated value for h with the reported initial flux, the absorption takes place too rapidly, and the difference cannot be countered by changes in the other parameters. Stress relaxation was thought to be the origin of this "anomalous" behavior by Hopfenberg and coworkers. Stress relaxation is a bulk phenomenon. If this is the proper explanation a calculated average *effective* (constant) diffusion coefficient, D_{ave}, that would essentially saturate a 1½ mil free film after about 800 hours can be estimated with $D_{ave}t/L^2 = 1$ as $1.25(10)^{-14}$ cm^{2}s^{-1}. This relation is based on the solution to the diffusion equation for a constant diffusion coefficient for absorption to 95% of the equilibrium value [28]. This *effective* diffusion coefficient would have to prevail as an average in the experiment no matter which theory is applied to explain behavior based on bulk phenomena

alone. The effects of a stress relaxation mechanism, for example, would have to delay the rate of transport by a factor of at least 100 compared to the D_0 assumed in the modeling. The effective local diffusion coefficient would have to be lower than this at the lowest local concentrations and somewhat higher at the highest. This would imply a speeding up of the absorption process at the longest times, a situation not supported by the asymptotic approach to equilibrium. The significant surface condition explanation does not have this problem as it quite satisfactorily explains the asymptotic approach to equilibrium as a result of the reduced concentration difference across the surface. These considerations alone would seem to render most, if not all, prevailing theories of "anomalous" diffusion, where control is within the bulk of the polymer, as being extremely doubtful.

Other experiments involving Super Case II behavior that have been modeled by the methodology discussed here include a fictitious example in [5] and the absorption of methanol into PMMA at 0°C [29]. There are a variety of conditions that can give this type of behavior.

It is concluded Super Case II absorption behavior is also modeled satisfactorily by the diffusion equation with concentration dependent diffusion coefficients and a (very) significant boundary condition. The general behavior is clear, but details can, of course, vary from case to case.

7. A special case

Finally, the very special case of liquid dichloromethane absorption into stretched and constrained cellulose acetate films is discussed in response to a challenge that a given experiment could not be modeled in the way advocated here [30]. The explanations are all given in terms of stress relaxation in [30] and in previous studies of Petropoulos and coworkers. This does not seem necessary based on the present treatment. The experiment in question studied the absorption from liquid dichloromethane into a nominally 1 mm thick cellulose acetate film that was stretched in one direction and then confined between two glass microscope slides [30,31]. This allowed for absorption both parallel and perpendicular to the stretching direction. The absorption is modeled in Fig. 6 for the perpendicular absorption case and in Fig. 7 for absorption parallel to the direction of stretching. The constrained equilibrium concentration is 0.26 volume fraction compared with 0.73 volume fraction for the unconstrained case.

The diffusion into the stretched and constrained cellulose acetate film is much slower in the direction of orientation than it is in the perpendicular direction. The reason for this is thought to be that moving a polymer molecule, or significant segment thereof, is required for diffusion to occur. Cellulose from wood pulp has typical chain lengths between 300 and 1700 glucose units. The polymer chains are very stiff. It would be reasonable to assume that many of these would have associated many times with neighboring molecules in the stretching direction, whereas much fewer of such "physical bonds" between polymer chains would be found in the perpendicular direction. It much easier to move the long, stiff molecules in the "across" direction, and diffusion of molecules whose size resemble that of a glucose unit need not go so

deeply into the bulk before significant polymer segment motion is possible. The modeling of this in Fig. 6 confirms that there are no special considerations to be taken for absorption perpendicular to the direction of orientation with the diffusion equation being able to model the process.

The experimental concentration gradients given in Fig. (8c) of [30] for diffusion perpendicular to the direction of orientation for this experiment are matched in Fig. 6. These gradients are also matched by data for absorption into semi-infinite media with exponential diffusion coefficients that vary in the range of interest between a factor of 95 and 200 given by Crank [32]. The experimental time for the front to reach 0.8 mm is about $t^{1/2}$ equal to 9.5 $min^{1/2}$, which is equally matched by the linear curve at the lower right in Fig. 6. There is no significant surface mass transfer coefficient for entry in the perpendicular direction. The value of h used in the figure is not necessarily the right one, having been set too high to have significance.

In the stretched direction a much larger number of solvent molecules must enter the polymer in order to provide appropriate polymer mobility for significant diffusion. The required depth of penetration of solvent is only a few "glucose units" in the across direction to provide the concentration dependent diffusion. The "distance" in the direction of orientation for this may be as much as several hundred "glucose units" before a cellulose molecule is "freed" sufficiently to allow very rapid diffusion at very much higher concentrations behind the advancing front. There must be appreciable uptake of solvent before the polymer chains can move suitably. When this is achieved, the motion will be dramatic because the concentration is so high just behind the moving front. This process can continue with successive polymer molecules being "freed", and the front moves through the film. This physical model then allows for a very high diffusion rate behind a very sharp advancing front as seen in Fig. (8c) in [3] and in Fig. 7.

The diffusion coefficients used to model absorption in the direction parallel to stretching are assumed to be constant at $2(10)^{-13}$ cm^2s^{-1} at concentrations less than 0.05 volume fraction. This concentration was found by trial and error to duplicate the position and shape of the experimental precursor. Above this concentration an exponential increase is assumed with a maximum value at the surface concentration equal to $1(10)^{-5}$ cm^2s^{-1}. There is a moderately significant surface mass transfer coefficient that leads to the two stage absorption curve. This h is also in agreement with the data in Table 1, but the agreement may be fortuitous. The absorption curve matches that reported in Fig. (8a) in [30]. The concentration gradients clearly show an advancing front, although not as sharp as that in Fig. (8c) in [30]. In view of the simple modeling approach, this is judged satisfactory to demonstrate the viability of the physical model discussed above. A reason for there being more solvent in the film at the highest concentrations behind the experimental sharp front can be because of the inability to control what happens at the exposed surface. The stiffness of the sample in the oriented direction may prevent the adequate sealing against the glass that would be more easily found in the perpendicular direction. There may also be non-uniform swelling of the exposed surface into the liquid. The modeling here emphasizes a perfect match of the precursor as being more interesting, perhaps at the expense of a sharp advancing

front, whereas the modeling in [30] emphasizes matching the sharp front, with somewhat less satisfactory matching of the precursor.

The following was added on October 5, 2013:

"The data reported for the very flat top of the step in the experiment with absorption parallel to the stretching direction can be used to measure the effective diffusion coefficient that gave this experimental result. The constant flux is given and a reasonable estimate for the concentration gradient can be gotten by expanding the figure. The resulting diffusion coefficient using Fick's first law is several times larger than the self-diffusion of the liquid dichloromethane itself. The experiment is thus inappropriately interpreted. There has been considerable leakage in the direction of the stretching, thus making proper interpretation impossible. In the modeling diffusion coefficients higher than that expected for self-diffusion in pure dichloromethane were not allowed."

It is concluded that the diffusion equation with suitable boundary conditions and diffusion coefficients profiles can match the experimental data reasonably well, and that reference to a stress relaxation model is not required. But how can the modeling of Petropoulos and coworkers give such good agreement with the experimental results? This is discussed below.

8. Desorption

Film formation by solvent evaporation is essentially desorption starting at some relatively high solvent concentration sufficient to give a viscous liquid that can be applied as a wet film. The whole process can modeled by the diffusion equation and be divided into two phases [1,6]. In the first phase there is still solvent at the air surface, so the boundary condition given in Eq. (2) is significant. In the second phase it is diffusion in the bulk of the film that controls further desorption. Fig. 8, reproduced from earlier publications [1,6], since it contains so much additional information, clearly shows the two phases. The diffusion coefficients that were used are discussed in some detail in [1,2,5] and are given in Fig. 2 at the upper right. They were determined in a closed apparatus with control of the partial pressure of the solvent being studied. Stepwise absorption was employed as was desorption from different uniform initial concentrations. The methodology for analyzing such data is given in [1,2,5]. This accounts correctly for concentration dependence as well as a significant surface condition in absorption if required. All of these experiments gave consistent results. Film drying was followed for about two years in a climatized room. This allows the absorption of some plasticizing water. After the initial publication of Fig. 8 data not shown were obtained by desorbing under vacuum for several months. The rate of desorption followed exactly that given as "calculated" in Fig. (8).

It can be concluded that the diffusion equation can successfully model film formation. It has also been used to analyze desorption data giving results agreeing with absorption data. This would seem impossible with a model based on stress relaxation or related phenomena.

9. Permeation

Permeation data for protective gloves (steady state permeation rate, breakthrough time, time-lag) have collectively been matched in chapter 17 of [3] for numerous systems with different glove types and challenge chemicals by assuming reasonable diffusion coefficients until the calculated results match the data reported in the literature [33,34]. An example of this is given in the following.

The breakthrough time reported in Fig. 9 is for the concentration at the exit surface reaching 0.1 times the equilibrium concentration. The ASTM breakthrough time is defined as the time at which a steady state permeation rate of $1.67(10)^{-9}$ $gcm^{-2}s^{-1}$ is attained. These same units for permeation rate are used in Fig. 9. The lower blue curve at the lower right gives the total amount of solvent taken up relative to the final value, and the upper red curve gives the permeation rate at the given time, showing a breakthrough and final steady state rate. Values can be read on the screen for purposes of interpolation.

Fig. 9 models methylene chloride permeation in Viton® gloves using data from [34]. This is a very careful and thorough study providing the data needed. The agreement is excellent with the reported ASTM breakthrough time of 38.4 min being matched with 38.3 min, and with the reported steady state permeation rate $1.15(10)^{-6}$ $gcm^{-2}s^{-1}$ being matched with a calculated value equal to $1.13(10)^{-6}$ $cm^{-2}s^{-1}$. The diffusion coefficients assumed seem reasonable for a small molecule diffusing in an elastomer, but such modeling should be confirmed by actual measurement of diffusion coefficients wherever possible. The concentration gradients in the lower left of the figure confirm that the concentration at the exposed surface rises immediately to the equilibrium value as is generally assumed.

10. Discussion

The diffusion equation, Fick's second law, can correctly model experiments that otherwise have been called non-Fickian when the boundary condition given in Eq. 2 is used. The usual practice of assuming the surface concentration immediately rises to the final value is clearly incorrect in many commonly encountered cases. The surface concentration rises at a rate determined by solution of the diffusion equation for the relevant coefficients for surface mass transfer and diffusion. This rate need not be exponential nor in any other predetermined fashion, but the exponential rate is what is expected when this boundary condition becomes dominant with relatively low h values that remain constant or reasonably so.

Use of Eq. 2 is mandatory when there is significant resistance to mass transfer in the external phase as evidenced by an S-curve or other deviation from absorption with linear uptake using a plot with the square root of time. There is still a lack of understanding of the surface mass transfer coefficient since it can be affected by so many different factors. For example, it can be difficult to determine the relative significance of diffusion in the external phase to the polymer film surface, air currents at the sample surface, the vapor pressure of the given solvent, etc., or

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whether a significant h is due to the required heat transfer to provide the latent heat of evaporation in desorption experiments or to remove the latent heat of condensation in absorption experiments. All of these effects would be simultaneously included in the present treatment by the h coefficient in Eq. 2. It may be possible to separate them by careful experiment.

To complicate matters still further there are additional experiments, such as those called Case II or Super Case II, where the external factors discussed above cannot be significant in retarding absorption but where there is still a significant delay. It has been shown by examples in the above that solutions to the diffusion equation using the boundary condition given by Eq. 2 with a constant h can model these "anomalous" situations. It is postulated here that passage of the absorbing molecules through the surface itself into the bulk controls the absorption process in such cases. After adsorbing, a given molecule must orient correctly at a suitable site where it can be accommodated in such a way that entry into the bulk is possible. This is not a new thought. This kind of thinking led Skaarup [2,35] to postulate that once a given molecule was in a suitable position, h was proportional to the local diffusion coefficient to reflect its ability to move into the bulk. The ability to find such a suitable position was assumed inversely proportional to the minimum cross-sectional area of the given molecule, understanding that the shape would also have an effect. Thus, movement into the bulk is determined by the local diffusion coefficient and the concentration in the bulk just below the surface as given by Eq. 2, once the molecule resides properly in the surface. This does not explain why a constant surface mass transfer coefficient gives adequate modeling as shown in the above examples. It is further postulated in continuation of the discussion above that when a solvent molecule does move into the bulk, the polymer chains in the surface return to their previous conditions. This means subsequently adsorbing molecules will face the same entry problems as those that have already passed through to the interior of the film, and h will remain substantially constant. This is plausible based on the reasoning in the following.

The surface of the polymer sample will try to orient to reduce its surface free energy. The orientation is presumably one with the lowest attainable surface energy for the given conditions, and this can be expected to be as "hydrocarbon" in character as polymer chain segment motion allows when an air surface is involved. This initial orientation will also depend on prior history with such effects a cooling rates, annealing processes, and storage conditions (temperature and humidity) being important. Upon contact with a solvent the HSP of the polymer surface will determine how the solvent orients upon adsorption. The polymer chain segments can move only slowly compared with the essentially immediate potential for a solvent molecule to move while trying to find the best match of its local HSP to the local HSP of the polymer. The ability to experimentally assign HSP to the surfaces of solid materials such as pigments, carbon fibers, quantum dots, graphene, etc. [3] supports the concept that segments of adsorbing molecules preferentially adsorb onto chain segments of polymers that have similar HSP.

In the case of methanol and PMMA, the mechanism postulated above means the methyl group of the methanol will preferentially orient toward the PMMA surface, which is presumably

dominated by a hydrocarbon character. The extent of this can depend on several factors as discussed above and evidenced by the cooling rates and time lags found by Windle [20], for example. The preferred direction of entry, however, is with the alcohol group leading since this is smaller than the methyl group. The preferred orientation for entry into the bulk is opposite to the orientation for the presumed preferred adsorption. Such adverse conditions for entry are thought to be more probable when a solvent is only partially soluble in the polymer in question. The very fact of dissimilarity in the HSP, for example, suggests a certain degree of rejection. Entry will be hindered not only because of the greater dissimilarity in the HSP, but also because fewer suitable sites for absorption can be expected because of low solubility in the polymer in the first place. These factors are thought to be the background for the significant h in the Case II studies of Thomas and Windle modeled above. The fact that the time for equilibrium uptake for methanol is essentially identical for the time for the iodine tracer "fronts" to reach the middle of the free film at 30°C is in a sense regrettable. This was not the case at 62°C [17], but this was discounted in favor of another explanation that the iodine did closely follow the methanol. At the higher temperature the iodine did not exhibit a flat concentration profile. The iodine diffusion coefficients can be approximated from the data in the Thomas and Windle papers as being significantly lower than those of methanol [21]. The basis of Case II behavior as previously interpreted from these experiments appears to be in serious error.

Although data are acutely lacking on this point, there does seem to be some confirmation in Table 1 [13], that those solvents that absorb from the liquid state to the highest equilibrium concentrations have the highest apparent h values. The h value for tetrahydrofuran is so high as to make it insignificant in the absorption process studied. Neglecting this solvent, there is a linear semi-logarithmic tendency for the data in Table 1 for the smaller, more linear solvents but this does not include n-butyl acetate, which is too large and/or bulky for the comparison. It is also clear that solvents with still larger and/or still more bulky molecular structure will have still more difficulty entering the polymer. This is borne out in [13], where solvents having benzene rings simply could not enter the COC polymer Topas® 6013 (Ticona) in spite of HSP that predict that they should. These data confirm that h may take on a very wide range of values from high enough to be insignificant, in the case of tetrahydrofuran, $1.89(10)^{-4}$ cms^{-1}, to zero for solvents with a single benzene ring. It is concluded here that low equilibrium solubility can lead to lower surface mass transfer coefficients thus providing an additional barrier effect to that of lowered diffusion coefficients in the bulk of the film. Low equilibrium solubility implies a mismatch of HSP.

The stress relaxation approach of Petropoulos and coworkers uses a "kinetic" modulus, $\beta L^2/D$. According to [30], D/L^2, the diffusion coefficient divided by the film thickness squared, governs the diffusion rate, and β is the rate parameter ("relaxation frequency" = reciprocal relaxation time) of a swelling volume relaxation process described by

$$\partial C/\partial t = \beta(C^{eq} - C) \tag{4}$$

C^{eq} is the final concentration and C is a local concentration, which for moderate values or high values would approximate the surface concentration, C_s. Diffusion within the film is often so rapid at such concentrations as to essentially equalize the concentration in the film. The β used by Petropoulos and coworkers as a rate parameter for stress relaxation with a "kinetic" stress relaxation modulus can also describe the rate of exponential increase of the surface concentration during absorption to higher solvent concentrations as suggested by Long and Richman [36]. Eq. (4) used by Petropoulos and coworkers and Eq. (2) used by Hansen are essentially identical for given conditions, if not completely so, with β (adjusted for film thickness) approximating h, or vice versa depending on one's viewpoint. These equations give similar results, but the interpretation is quite different. The surface mass transfer coefficient can normally be measured in the laboratory or found by curve fitting as in the above.

One is forced to decide whether the "anomalous" behavior in absorption is from phenomena within the film if one believes in stress relaxation and related phenomena are controlling, or whether the surface effects described here are the reason(s). It would appear impossible for any theory based on bulk phenomena alone to satisfactorily model all of absorption, desorption, film drying, and steady state permeation.

11. Conclusion

The diffusion equation has been shown to satisfactorily model absorption, desorption, and permeation experiments in polymers including those otherwise called "anomalous". The successes of the simple solutions to the diffusion equation in all of the cases discussed here, including those frequently cited as being typical of Case II and Super Case II, for example, forces one to accept its expected generality, even for diffusion in polymers. There is no need to invoke stress relaxation, mechanical, or related theories that affect bulk properties to explain the observed phenomena.

The practical message that can be derived from this study is that maximizing differences in HSP will enhance barrier properties. Not only will this reduce the overall concentration gradient across a polymeric barrier, but it also lowers the maximum diffusion coefficient in the bulk of the film. Mismatches of HSP may also contribute to additional barrier effects at the surface. In special cases the surface itself is the barrier, especially for larger and more bulky molecular species.

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Table 1

Apparent surface entry mass transfer coefficients and equilibrium uptake for solvents in a COC polymer Topas 6013® (Ticona) as reported in [13]. Added on October 5, 2013: A plot of these data is given in Figure 10.

Solvent	Apparent h, cms^{-1}	Equilibrium uptake, volume fraction
Tetrahydrofuran	$1.89(10)^{-4}$	0.676
Hexane	$7.78(10)^{-6}$	0.351
Diethyl ether	$1.21(10)^{-6}$	0.268
Propylamine	$1.49(10)^{-7}$	0.181
Ethylene dichloride	$1.18(10)^{-7}$	0.176
Ethyl acetate	$1.46(10)^{-8}$	0.076
n-Butyl acetate	$8.30(10)^{-10}$	0.202
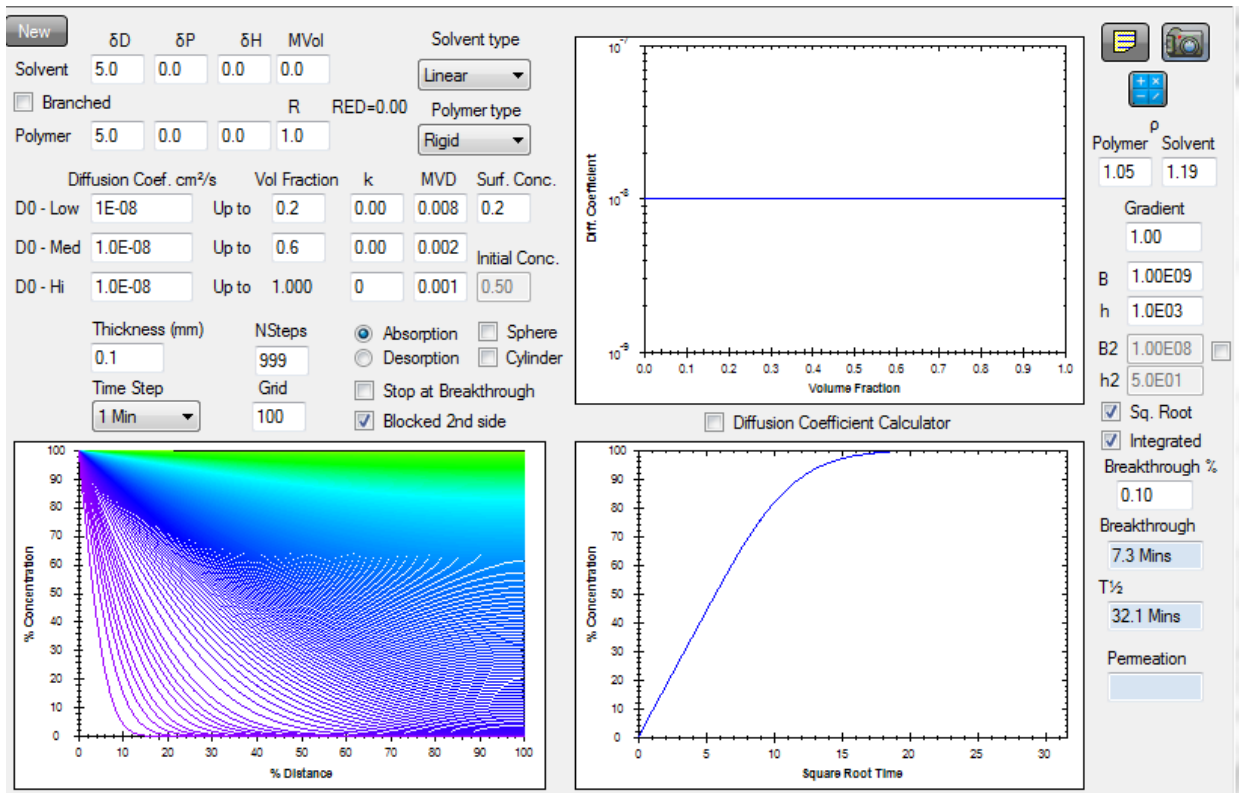
Figure 1. Absorption with a constant diffusion coefficient.
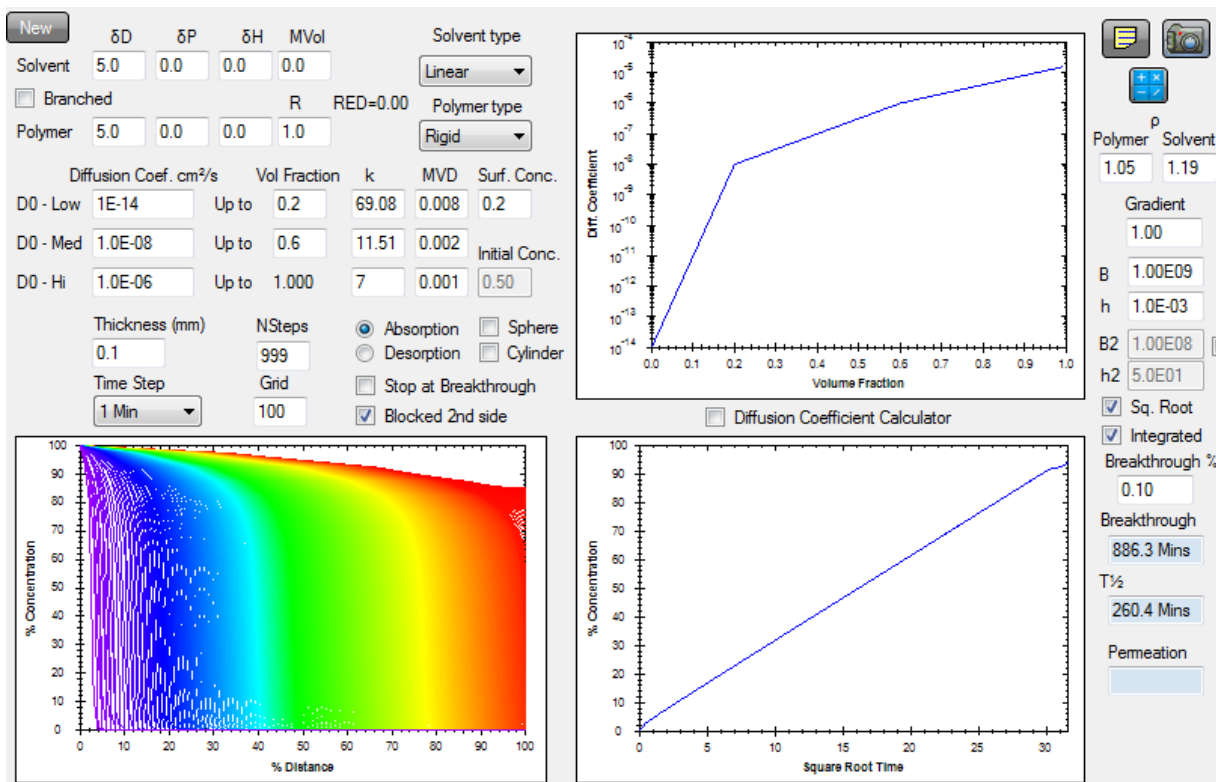
Figure 2. Model calculations for absorption in the rigid polymer region using carefully measured and concentration dependent corrected diffusion coefficients for chlorobenzene in poly(vinylacetate) at 25°C [1,2,5]. These diffusion coefficients reflect the general behavior of rigid polymers showing a rigid region at low concentrations, a rubbery region at intermediate concentrations, and viscous liquid-like region at the higher concentrations. These diffusion coefficients were also used to model film drying by solvent evaporation in Fig. 8.
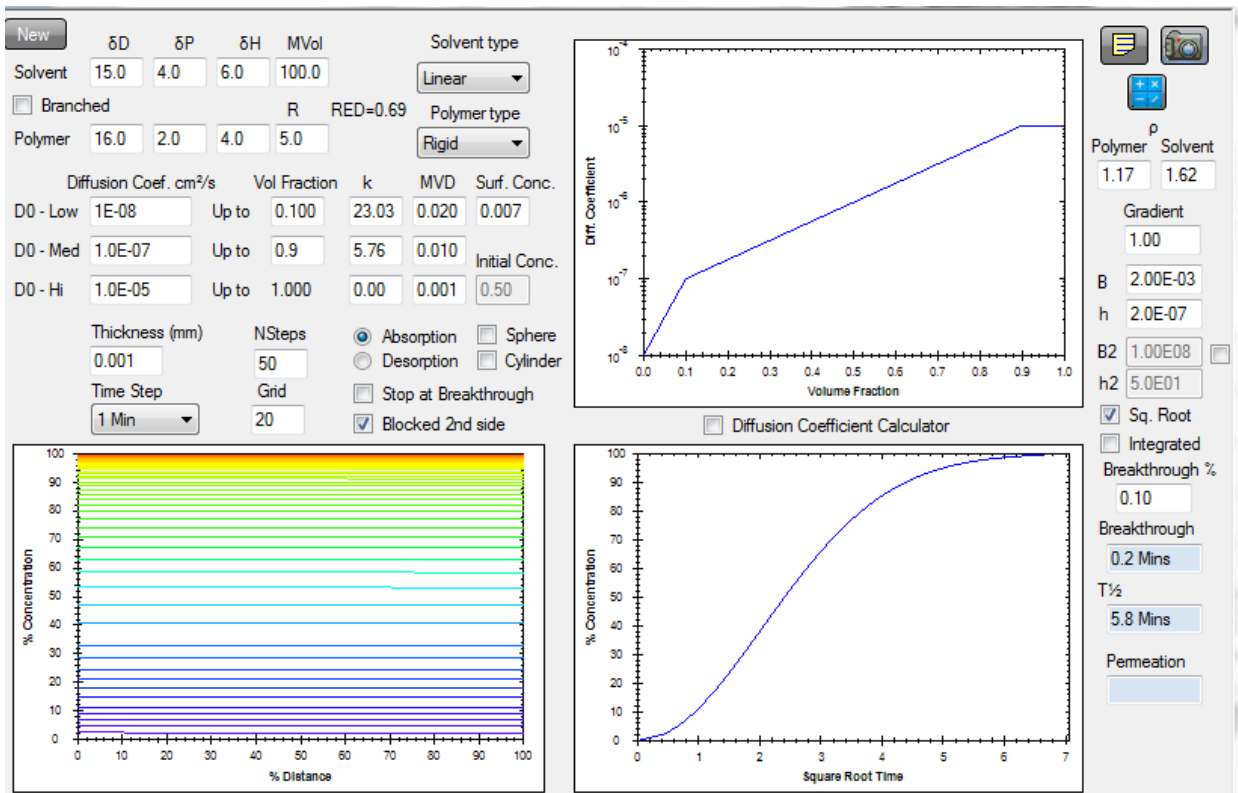
Figure 3. Modeling the uptake of supercritical carbon dioxide into a 1 micron thick film of PMMA on a quartz microbalance. Data from [10].
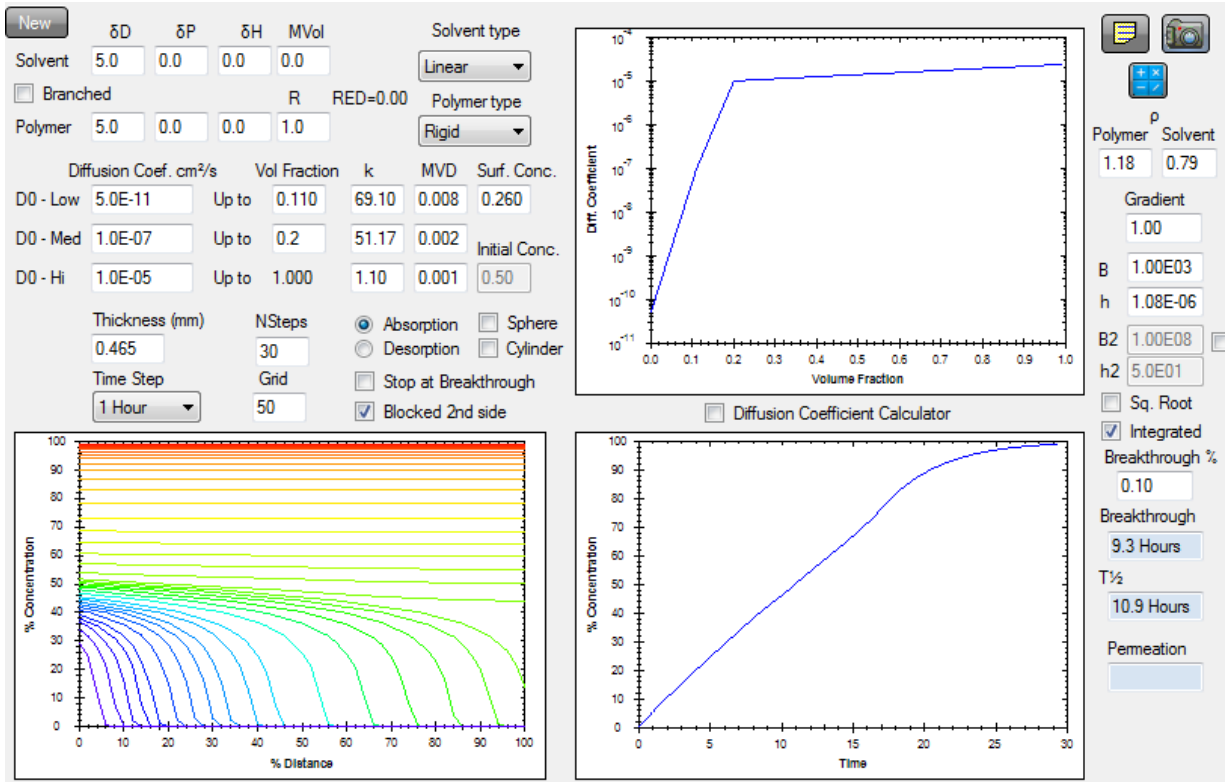
Figure 4. Modeling typical Case II absorption of methanol into PMMA at 30°C using data from Thomas and Windle [14,17]. The absorption curve at the lower right matches the experimental data as a straight line on a plot using linear time, but the concentration gradients are very far from a step-like advancing front as indicated by Thomas and Windle. The iodine tracer method used in this study is not suitable to follow the diffusing methanol with misleading conclusions as a result. The data in [14,17] confirm that Iodine diffuses much more slowly than methanol.
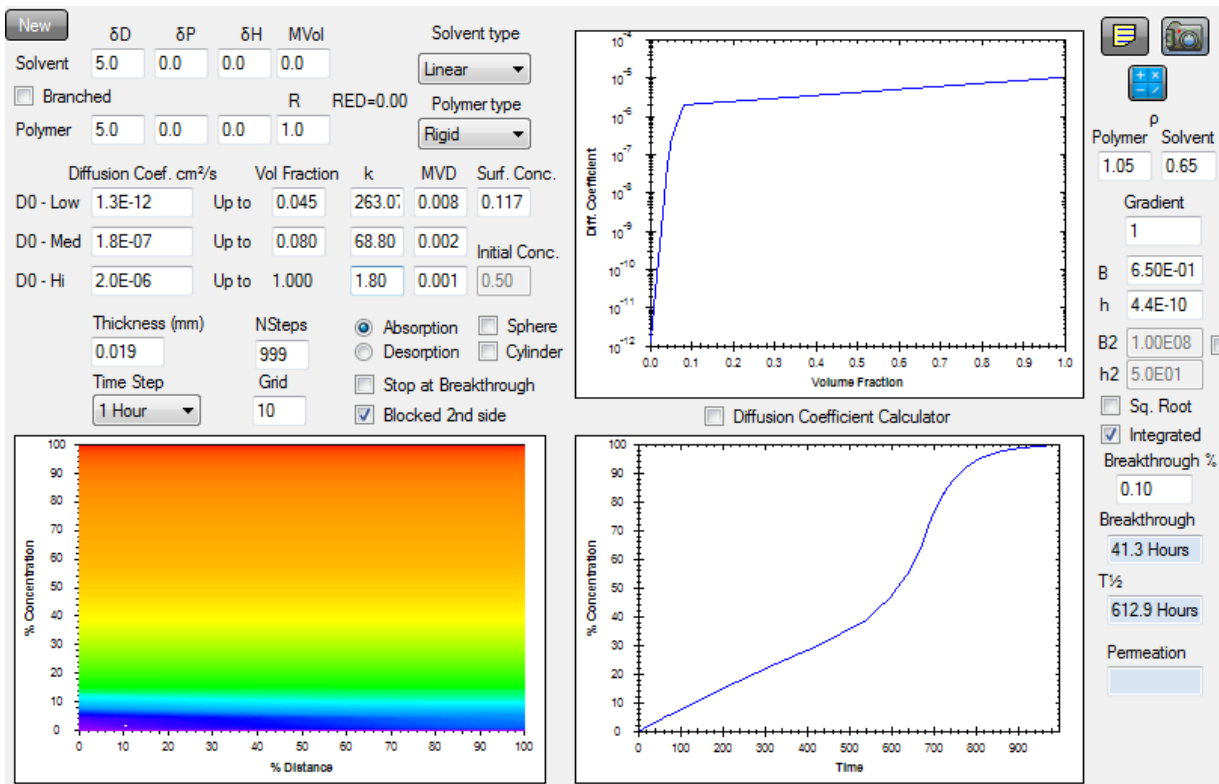
Figure 5. Model for the absorption of n-hexane into polystyrene using data from [23,24]. The experimental absorption curve with sharp upward curvature on a plot using linear time is matched at the lower right. The concentration gradients are flat almost from the start showing the surface condition determines the rate of absorption, although the upward curvature is very sensitive to the diffusion coefficient profile.
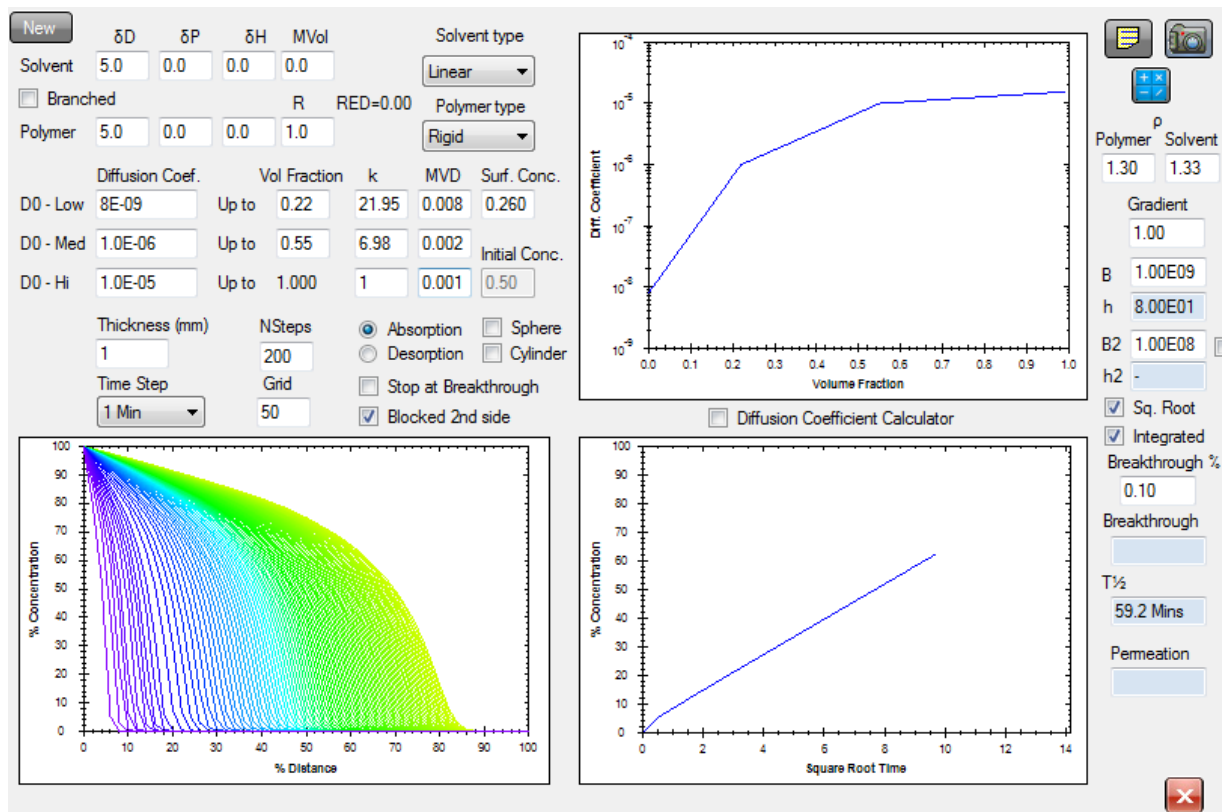
Figure 6. Model using the diffusion equation for absorption with liquid contact of dichloromethane into a restricted, stretched cellulose acetate film perpendicular to the direction of orientation. The experimental data being modeled are given in [30,31].
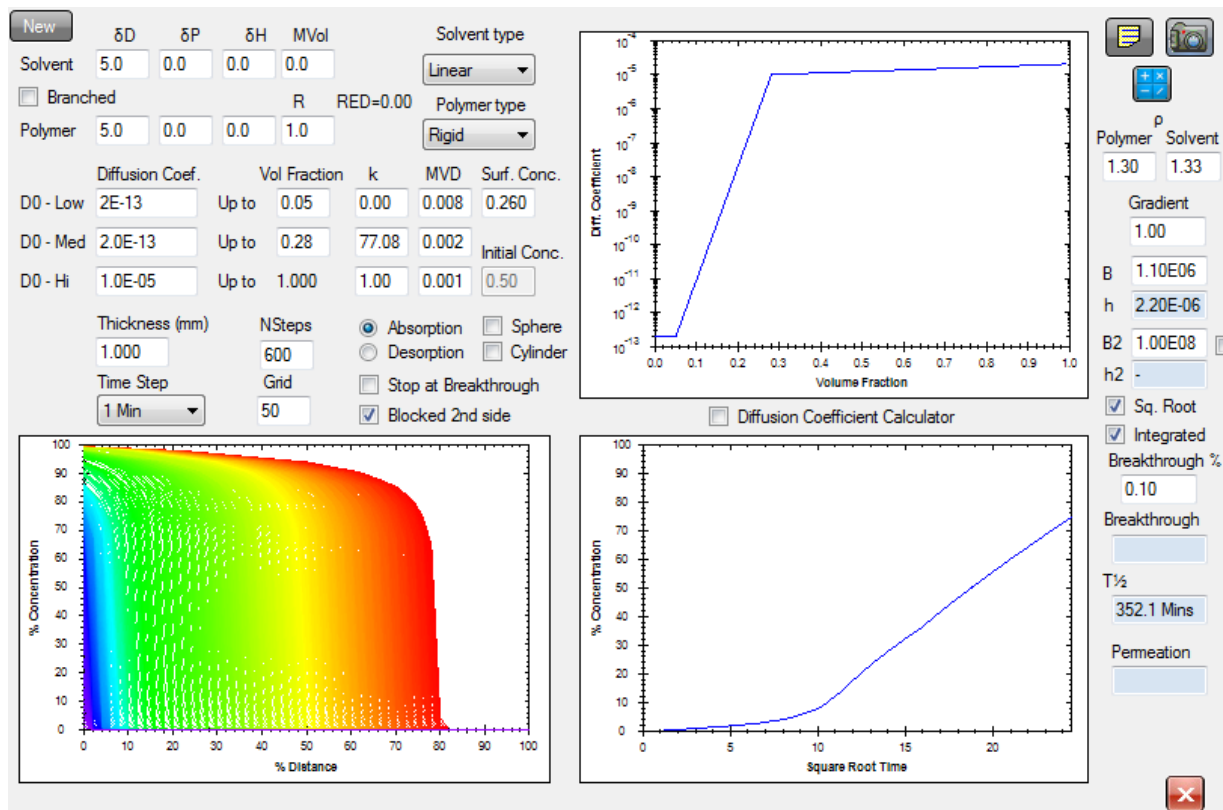
Figure 7. Absorption of dichloromethane into an oriented cellulose acetate film in the direction of orientation using data from [30,31] as modeled by the diffusion equation with a moderately significant surface mass transfer coefficient and diffusion coefficients found by trial and error based on considerations discussed in the text. The following added on October 5, 2013: The experimental diffusion coefficients based on the data in [30,31] are much larger than the expected self-diffusion coefficient for dichloromethane used in this figure. There was obviously a poor seal against the microscope slide in the stretched direction.
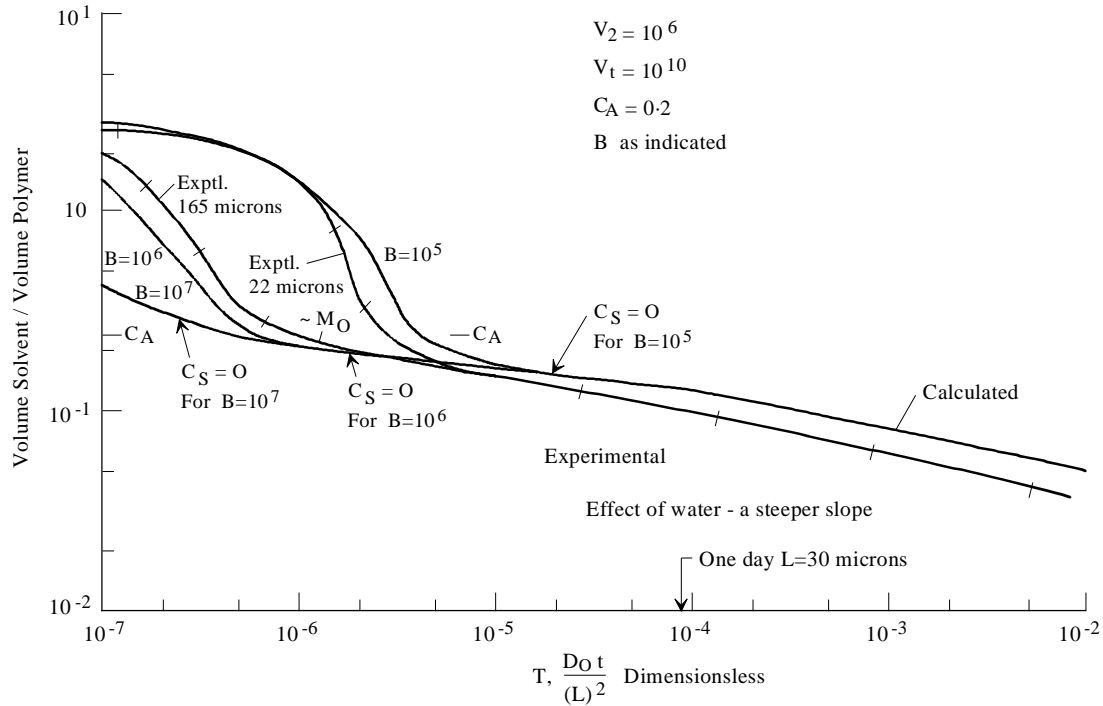
Figure 8. Calculated and experimental drying curves for the evaporation of chlorobenzene from polyvinyl acetate at 25°C [1,6] showing two phases. Film drying in a climatized room was faster than film drying in a vacuum apparatus, where diffusion coefficients were measured. The calculated and measured curves under vacuum coincided at long times. The diffusion coefficients used are those in Fig. 2.
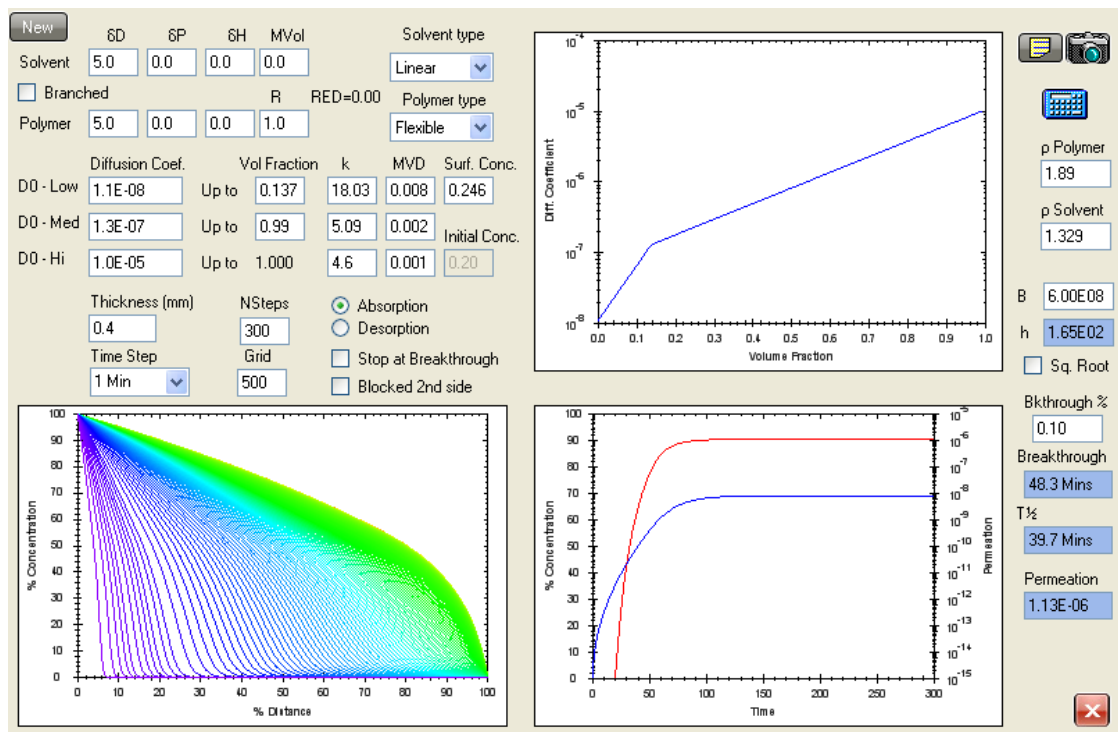
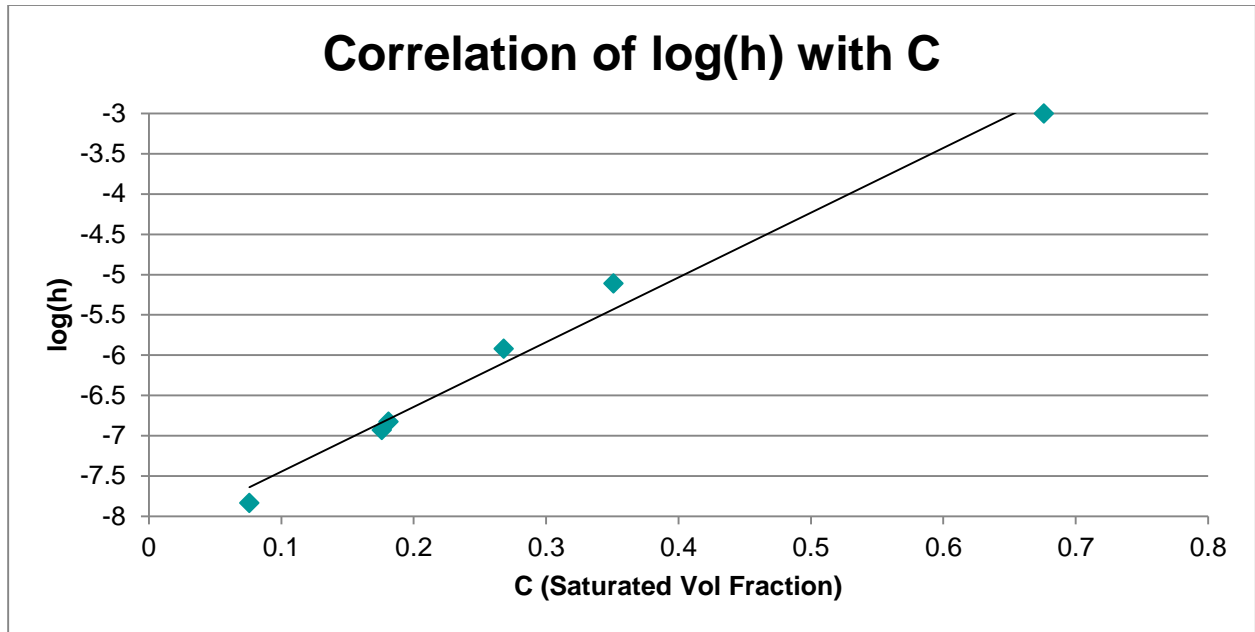Figure 9. Permeation of methylene chloride in Viton® chemical protective gloves matching permeation data from [34].

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