

Surface Effects versus Bulk Phenomena as Explanations of “Anomalous” Absorption in Polymers

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Abstract

Problems with explanations for diffusion in polymers based exclusively on bulk phenomena are contrasted with successful modeling provided by the diffusion equation itself. None of the theories exclusively based on bulk phenomena are satisfactory. The parameters used in the successful diffusion equation modeling have either been measured or can be verified experimentally. A significant surface boundary condition is required to model the absorption curves for what is called “anomalous” diffusion including sigmoidal (two-stage), Case II, and Super Case II. Sigmoidal absorption need not necessarily include diffusion coefficients that depend on solute concentration, while Case II and Super Case II require these. Exponential dependence of the diffusion coefficients on solute concentration has been used successfully, sometimes requiring many decades of change in the same experiment. The exponential dependence is expected theoretically and has been confirmed earlier by the agreement of absorption and desorption experiments when data were treated properly. The initial delay characteristic of sigmoidal absorption is explained by the relative importance of the surface resistance and the diffusion resistance. In some cases diffusion resistance dominates initially, but subsequently can completely lose importance as the solute concentrations and diffusion coefficients increase with higher concentration. In other cases, for example those with constant diffusion coefficients, the diffusion resistance increases moderately as absorption proceeds and can exceed the surface resistance, thus allowing the surface concentration to ultimately reach the equilibrium value after slowly rising from the start. For Case II and Super Case II increasing solute concentration means the diffusion resistance becomes less and less important as absorption proceeds. While diffusion resistance may have initial importance, this decreases with continued absorption. The final stages can be completely dominated by the surface condition because of a very low concentration difference between the film surface and the external phase. The surface mass transport coefficient can also be important for liquid contact. An entry mass transfer coefficient for smaller molecules correlates very well with their equilibrium uptake for a COC polymer. This indicates the number of available sites allowing adsorption, orientation, and absorption strongly affects this coefficient, although large molecular size or irregular shape can slow or even completely stop absorption in spite of expected solubility. These results and the fully satisfactory modeling of various kinds of “anomalous” absorption with the diffusion equation exclude any explanation exclusively based on effects in the bulk.

A more complete analysis [1] based on earlier reports [2-6] is given elsewhere. Diffusion equation interpretations are given and contrasted with what is found in the literature. Examples include absorption to high solute concentrations and the lack of step-like concentration gradients in at least some of the frequently cited examples of Case II and Super Case II experiments.

Introduction

Interpretations of “anomalous” absorption phenomena in polymers exclusively based on bulk phenomena are widespread in the relevant literature. A review by Vesely discusses the main theories derived from absorption experiments [7]. He finds them incomplete and provides a new approach by correlating a slowly rising surface concentration with an empirical equation. There is a simple, alternative explanation to all of these based on the diffusion equation solved with well defined, measured, and/or verifiable parameters. Explaining the “anomalies” for absorption requires a significant surface condition in particular and most often (exponential) concentration dependent diffusion coefficients. It has been felt necessary to deal with the diffusion equation approach in the introduction in order to have a basis for the criticism that follows. A key element in the diffusion equation approach is the need to consider the surface condition in the solutions modeling “anomalous” absorption, in particular. It may or may not be significant depending on the given circumstances.

The surface condition is given by Equation 1:

$$F_s = h(c_e - c_s) = -D(c)dc_s/dx \quad (1)$$

For absorption this equation says that at any given time, the mass passing through the surface that comes from the exterior phase, F_s , is equal to the mass passing through the surface into the bulk in the x direction. Preferred units are g/cm^2s for F , cm^2/s for diffusion coefficients, D , cm for x , and g/cm^3 (dry polymer) for concentrations, c . h is a surface mass transfer coefficient with units cm/s . The subscript s is for surface values. The subscript e is for final or equilibrium concentration values. These are most often the amount the film can absorb at equilibrium with a liquid solute, but can be the final amount taken up at some partial pressure of vapors.

The boundary condition given by Equation 1 is easily handled in numerical analyses by establishing an interval at the surface that does not contribute to the x distance. In this modeling both c_e and h have been kept constant with c_s being determined as time goes on in balance with what happens on the bulk side of the surface.

The surface resistance and the diffusion resistance are both present at the same time in series. Their relative importance can change as absorption proceeds. An immediate increase of the surface concentration to the equilibrium value inherently involves the assumption that the surface resistance is not significant relative to the diffusion resistance. The surface mass transfer coefficient has been or is assumed high enough to give this result. A constant surface mass transfer coefficient has provided quite good results for a wide variety of systems and different experimental conditions. A possible reason for this success is that the mobile polymer chain segments maintain a given orientation throughout an experiment as determined by the closest match possible in their Hansen solubility parameters (HSP) and the HSP of the external medium. This keeps the interfacial free energy as low as possible. More subtle effects can be found for liquid exposure in the surface itself. Passing through the surface can be limited or even stopped

by solute factors such as large molecular size and/or irregular shape. Low equilibrium solubility also means fewer suitable surface sites are available for the required adsorption, orientation, and absorption steps. This proposal is supported by the correlation in Figure 1 showing the equilibrium uptake and surface mass transfer coefficients are very strongly connected. These data are for different liquids of relatively low molecular volume absorbing into Topas[®] 6013 (Ticona) [4] at room temperature. The sample thickness was 0.9 mm. Equilibrium uptake also correlates with Hansen solubility parameters (HSP). A mismatch in the HSP of the solute and polymer gives low h and in given cases improves barrier properties beyond what is expected from lower concentration gradients and lower diffusion coefficients alone.

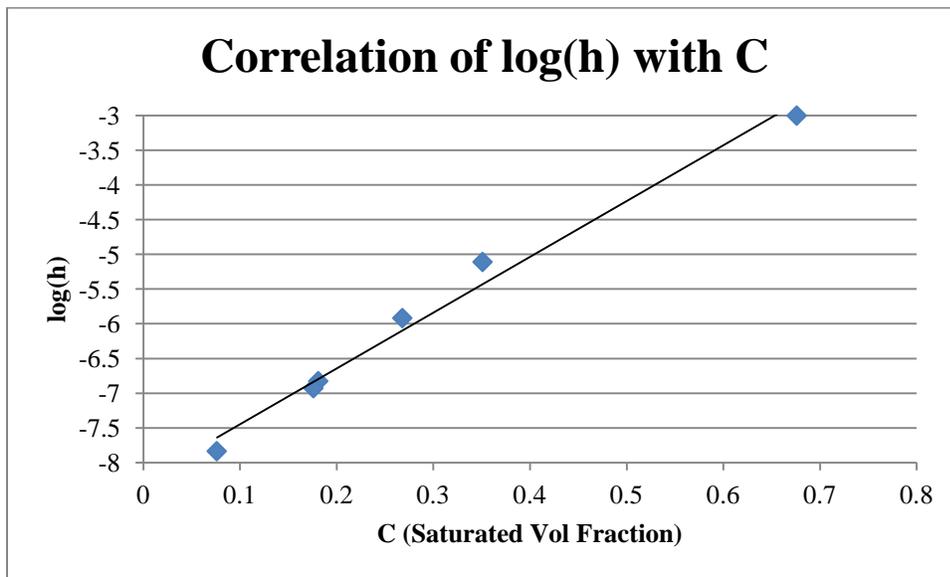


Figure 1 shows the importance of the equilibrium uptake for the surface entry mass transfer coefficient, h , for different liquids in Topas[®] 6013 (Ticona). The data are taken from [4]. The sample thickness was 0.9 mm. Lower equilibrium uptake is found for a mismatch in the Hansen solubility parameters (HSP). The figure confirms that a mismatch in HSP also contributes to good barrier properties by reducing h as well as reducing concentration gradients and diffusion coefficients.

It is felt that brief descriptions of how the diffusion equation models “anomalous” absorption are required to allow the comments and questions in the following relative to the problems of bulk phenomena explanations for these same processes.

Case II and Super Case II absorption

Case II absorption describes experiments where the absorption is linear with linear time. Super Case II absorption is similar to this, but the rate of absorption increases with linear time. These are called “anomalous” because they do not follow what is called “Fickian” absorption meaning

a linear rate of absorption when a plot using the square root of time is employed. Modeling with the diffusion equation has shown that Case II and Super Case II require considerable concentration dependence of the diffusion coefficient with the ratio D_{\max}/D_0 being several orders of magnitude or more. In addition a surface condition of significance is also required.

Increasing solute concentration means increasing diffusion coefficients when these vary with concentration. In such cases the diffusion resistance changes as absorption proceeds. The diffusion resistance may be significant or share significance with the surface resistance initially. As the precursor moves further into the film, there is a requirement for solute being transported over longer distances. After the precursors meet at the center of a free film, it starts to fill in a more uniform manner. The diffusion resistance decreases to such an extent at the higher concentrations that the surface condition takes a dominant role in the latter stages of absorption. An example is given in Figure 2 for the Case II data of Thomas and Windle that is considered typical for Case II [8-14]. The absorption curve is given at the lower right. The concentration gradients are given at the lower left. The diffusion coefficients assumed are reasonable based on literature data. These are given in the figure at the upper right as well as numerically at the upper left.

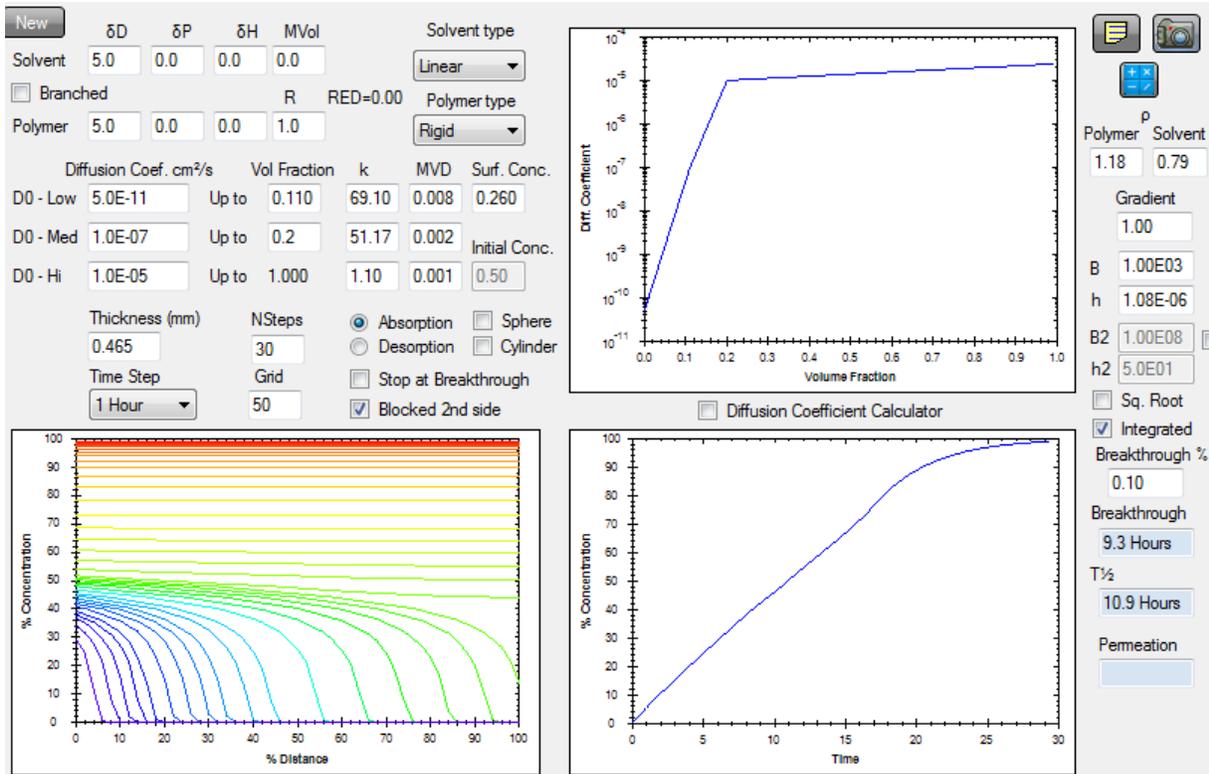


Figure 2 models the experimental data chosen by Windle in [8] for an expanded discussion of Case II absorption. These data are for the absorption of methanol into PMMA at 30°C. The linear uptake with linear time at the lower right matches the experimental Case II results. The methanol concentration gradients at the lower left are not sharp, advancing fronts as one is led to believe in the studies of Thomas and Windle. The diffusion coefficients given at the upper right are what can be expected for this system. Methanol “fronts” meet at the center of the free film after about 9 hours compared with the data for iodine used as a tracer where the “fronts” meet after about 23 hours. Unfortunately this is approximately the same time as the film reaches the maximum concentration of methanol. Step-like concentration gradients do not exist for methanol in this system according to this analysis based on the diffusion equation. A detailed analysis of the Thomas and Windle studies is given in [15].

There is no advancing step-like front in Figure 2 for the absorption of methanol into PMMA at 30°C as reported by Thomas and Windle [8]. An iodine tracer was used to follow the methanol. The iodine tracer has been shown to lag the methanol in the methanol swollen polymer in such a manner that it reaches the center plane of the free film after about 23 hours [15]. This is, perhaps unfortunately, also the same time as the methanol saturates the film. This coincidence is not found at higher temperatures. The studies of Thomas and Windle at different temperatures are also discussed in more detail in [15]. Super Case II examples from the literature are modeled successfully with the diffusion equation in [16]. Diffusion equation modeling has confirmed that

the “anomalous” absorption behavior of the types called Case II and Super Case II is caused by the relative importance of the diffusion resistance decreasing with increasing concentration as a result of the increasing diffusion coefficients. The surface condition is dominant at the later stages of these kinds of absorption experiments as can be seen, for example, from the flat concentration gradients in Figure 2. This analysis gives radically different results with horizontal concentration gradients toward the end of the experiment rather than vertical, step-like profiles indicated by Thomas and Windle. Any attempt to model a step-like concentration profile in such systems is an attempt to model an erroneous interpretation of the data.

Sigmoidal or two-stage absorption

There are different situations that can give sigmoidal (two-stage) absorption which inherently involves delaying the uptake at short times. A common mechanism is that the surface resistance causes a slowly rising surface concentration at the start, but as time goes on, the solute must diffuse farther and farther into the film, and this then becomes the dominant resistance. The surface concentration ultimately reaches the equilibrium value for the experiment well before the bulk of the film reaches the equilibrium value.

Another form of two-stage absorption has been reported for the absorption of supercritical carbon dioxide into 1 micron thick films of PMMA [17]. In this case an analysis based on the diffusion equation [18] showed that the surface condition dominated the whole absorption process that took 20-30 minutes. See also the discussion below.

Still another mechanism for two-stage absorption is found when diffusion controls at shorter times, but, similar to the Case II example above, it is no longer significant at longer times. A typical example of this kind is reported in [19] and reexamined in [6] for water absorbing into poly(vinyl alcohol) films from a bone dry condition to a very high final concentration.

It should be noted that a significant surface effect is present either initially or later in all of these situations.

Discussion

The discussion consists of a number of situations and questions that I believe favor a diffusion equation approach over that based on bulk property or mechanical explanations. The reader is free to make his or her own decisions, of course.

1. Perhaps the most convincing argument in favor of the diffusion equation approach is that it offers full explanations for all of the important phenomena including absorption (and the so-called anomalies), desorption, and permeation, using measured and/or verifiable parameters in an equation with a very general derivation. A general review of this is given in [6]. A more detailed and extended analysis is given in [1] with still more detail for the key issues referenced therein. I have not seen any theory based on stress related or

bulk mechanisms that can provide such guidance with potential courses of action, including the ready availability of easily used and suitable software [20].

2. Simple solutions to the diffusion equation can correctly interpret desorption and absorption experiments to give consistent exponential diffusion coefficients [2,3,5,6,21]. The methodology for correct interpretation of measurements of exponential diffusion coefficients is given in a number of places [2,3,5,21,22]. In my approach one basically compares half-times for the experiments with those found from solutions to the diffusion equation for different degrees of exponential concentration dependence. In these interpretations it is not the slope of the Log (diffusion coefficient) versus concentration that is important in a given experiment, but rather the ratio of the diffusion coefficient at the maximum concentration, D_{\max} , relative to that at essentially zero concentration, D_0 . Crank's method to correct the apparent diffusion coefficients involves multiple integrations [22]. Crank's approach gives the same result as that I have used, but it is somewhat more involved. Curve matching is also possible with solutions of the diffusion equation generated by the software in [20], for example.

The main point here is that if stress factors had been important, the diffusion coefficients found for absorption would not agree with those found for desorption. How would stress parameters be used to analyze desorption experiments? Parenthetically it should be noted that exponential diffusion coefficients are predicted from free volume theory. Reports of what I consider properly interpreted diffusion coefficient measurements in the literature are extremely rare, except when the diffusion coefficients are indeed constant. If there is an exponential dependence on concentration this must be included in interpretation of relevant data. It is my belief that this is the case for diffusion in polymers with increases of about 3 volume percent solute leading to an increase in the local diffusion coefficient by a factor of about 10 for rigid polymers.

3. Figure 1 shows that the surface mass transfer coefficient decreases exponentially with decreasing equilibrium uptake for small molecules in a rigid polymer. I do not see how any bulk theory can explain this important effect that is present at the surface from the very start of an experiment. These values are found from extrapolation to time equal to zero meaning no absorption has taken place yet.
4. Diffusion coefficients are not usually reported in studies of "anomalous" absorption that are explained by bulk theories. The same experimental data, otherwise interpreted by a mechanical or bulk theory, should be analyzed for the required *effective* diffusion coefficients that would reproduce the phenomena. In one case the *effective* (constant) diffusion coefficient was 4 orders of magnitude lower than what was expected for the diffusion coefficient of the solute in the given polymer [17,18]. Some effect has to delay

the uptake relative to what is commonly called “Fickian” diffusion with the “expected” diffusion coefficients. The mechanical approaches all attribute this delay to bulk effects of one kind or another. The diffusion equation approach attributes the delay in this case exclusively to a very significant surface effect. As discussed above there is a surface resistance in series with the diffusion resistance. When this delaying effect is correctly attributed to a surface effect, the diffusion coefficients in the bulk retain their reasonable and verifiable values that can be found in studies where the surface effect is not important. An *effective* constant diffusion coefficient can be estimated from the relation D_0t/L^2 . The solution for the diffusion equation with a constant diffusion coefficient and no significant surface resistance gives this quantity as equal to about 1.0, or slightly higher, depending on preference, when the absorption process is almost complete. L is the thickness of a free film exposed on two sides and the time is given by t .

To sum up the discussion on this point it is my contention that bulk explanations for delayed uptake are not correct in general if they lead to *effective* diffusion coefficients that are too low. I believe that the delay in “anomalous” absorption is more properly interpreted with the balance between surface related effects and diffusion resistance, thus retaining the expected diffusion coefficients in the bulk at all times and concentrations.

5. Film formation from reasonable solution concentrations leads to cooling of the film (even to the extent that water from the air can condense) and heat is required to evaporate the solvent. There is resistance to evaporation based on how fast heat can be supplied to the system as well as diffusion in the air above the film. For “corresponding” absorption started with essentially dry films and ending at the same higher solution concentrations, the same amount of heat must be removed from the system and the diffusion phenomena in the external medium will be also encountered. The diffusion equation approach incorporates these kinds of resistances into the surface mass transfer coefficient. A demonstration of how surface effects can dominate absorption at high solvent concentrations is given in [23]. Here a poly(vinyl acetate) film with dry film thickness 7.35 microns absorbed chlorobenzene vapors from an initial concentration of 0.433 volume fraction to a final concentration of 0.482 volume fraction in a closed apparatus. The observed average (constant) diffusion coefficient was $6.34(10)^{-10}$ cm^2/s . This had to be corrected by factors 1.2 for concentration dependence and 254 for surface effects based on the measured h equal to $3.4(10)^{-6}$ cm/s . The final value $1.9(10)^{-7}$ cm^2/s is precisely that expected for the higher concentration. Use of such experiments is not recommended for measuring diffusion coefficients, but they do demonstrate the importance of surface phenomena in absorption.

It may be possible to separate the different surface effects such as diffusion in a stagnant boundary layer, diffusion to the film in a closed apparatus from a remote source of

supplying new solute, heat transfer either to or from a film, and other effects, but this would require very careful and extensive studies.

- As shown above, there is no step-like advancing front in the frequently cited work of Thomas and Windle that is generally considered as being typical of Case II absorption. Any attempt to model a step-like absorption front in this system or similar systems is an attempt to model a thing that is not there. I therefore have to question the value of theories have been developed to do just this. I have also been motivated earlier by the studies of Thomas and Windle to try to model a step-like advancing front with the diffusion equation model. An approach to the sharp front could be found with very high ratios of D_{\max}/D_0 but the result was not 100% satisfactory if one seeks a 90° , step-like, advancing front. The result for D_{\max}/D_0 equal to $(10)^{10}$ is given in Figure 3. Typical absorption experiments may well encompass D_{\max}/D_0 equal to $(10)^7$ or $(10)^8$, so this example is not particularly exaggerated. A step-like advancing front was indeed found experimentally in one case as described in the next paragraph.

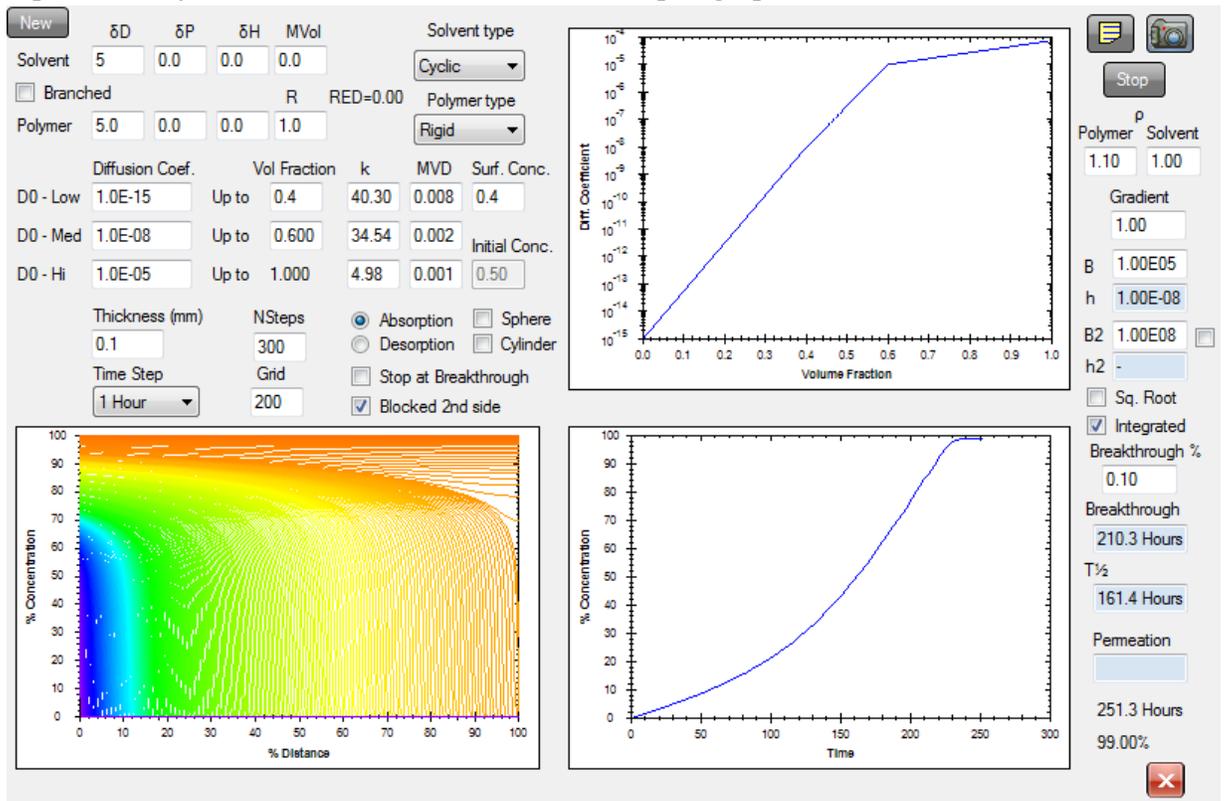


Figure 3 models Super Case II with extreme concentration dependence and a significant surface resistance. The upward curvature in the absorption curve at the lower right is indeed found with the surface condition being dominant at the end as shown by the flat concentration profiles at the lower left. While this typical of what gives Super Case II a sharp, step-like advancing front is not found. The same general kind of behavior for the

concentration gradients shown in Figure 3 has been found when modeling experimental Super Case II examples [16].

A very special experiment on a stretched, cellulose acetate film restricted between microscope slides demonstrated a step-like advancing front for absorption in the direction of stretching. The film was contacted with liquid dichloromethane in this study [24,25]. A bulk theory based on dynamic stress relaxation was given to explain the results. This experiment has been analyzed with the diffusion equation in some detail as reported elsewhere [1,26]. Absorption in the perpendicular direction is a simple case of concentration dependent diffusion coefficients with D_{\max}/D_0 equal to about 160 [1,26]. The concentration gradients and uptake curve in the perpendicular direction were those expected for this moderate degree of concentration dependence with assumed diffusion coefficients that were reasonable. The diffusion equation has been shown to model these results very well. No surface effect was required.

The absorption in the stretched direction was modeled with a constant diffusion coefficient up to 5% v solute in the cellulose acetate which has rigid polymer chains. This modeling suggests that the lengthwise oriented polymer chains have multiple points of association such that a given solvent concentration is required to separate them sufficiently for relatively easy motion. At concentrations above 5% v a rapid increase in the diffusion coefficient to the final concentration has been assumed as can be seen in Figure 4. The modeling confirmed that a value near 5% is required, not much more and not much less. The precursor was modeled accurately with these diffusion coefficients as was the uptake curve, but the step-like absorption front fell from about 80% of the maximum concentration rather than about 90% as found in the experiment. See Figure 4. It is thought that the sealing and perhaps other features of swelling at the liquid/film interface allowed slightly more solvent into the film than the assumptions of a uniform film exposed to the dichloromethane with excellent adhesion to the glass slides would provide. There is also the possibility of channeling between the oriented, stiff polymer molecules or other situation not in agreement with the assumed conditions at the highest concentrations. The assumed diffusion coefficients cannot be expected to be exact, but the major features of the experiment are well modeled by the diffusion equation. Surface resistance was also required to properly model this experiment for absorption parallel to the orientation of the polymer chains. This is not surprising since the polymer surface presumably consists largely of polymer chain ends where no absorption can occur, and these are rigidly held in place by neighboring chains. The modeling given in Figure 4 exactly matches the absorption curve and the precursor but not exactly the straight line concentration gradient at the highest concentrations. The modeling given in [24,25] matches the uptake curve with the step-like concentration gradients, but (perhaps) at the sacrifice of a rather poor match for the precursor at the lower concentrations.

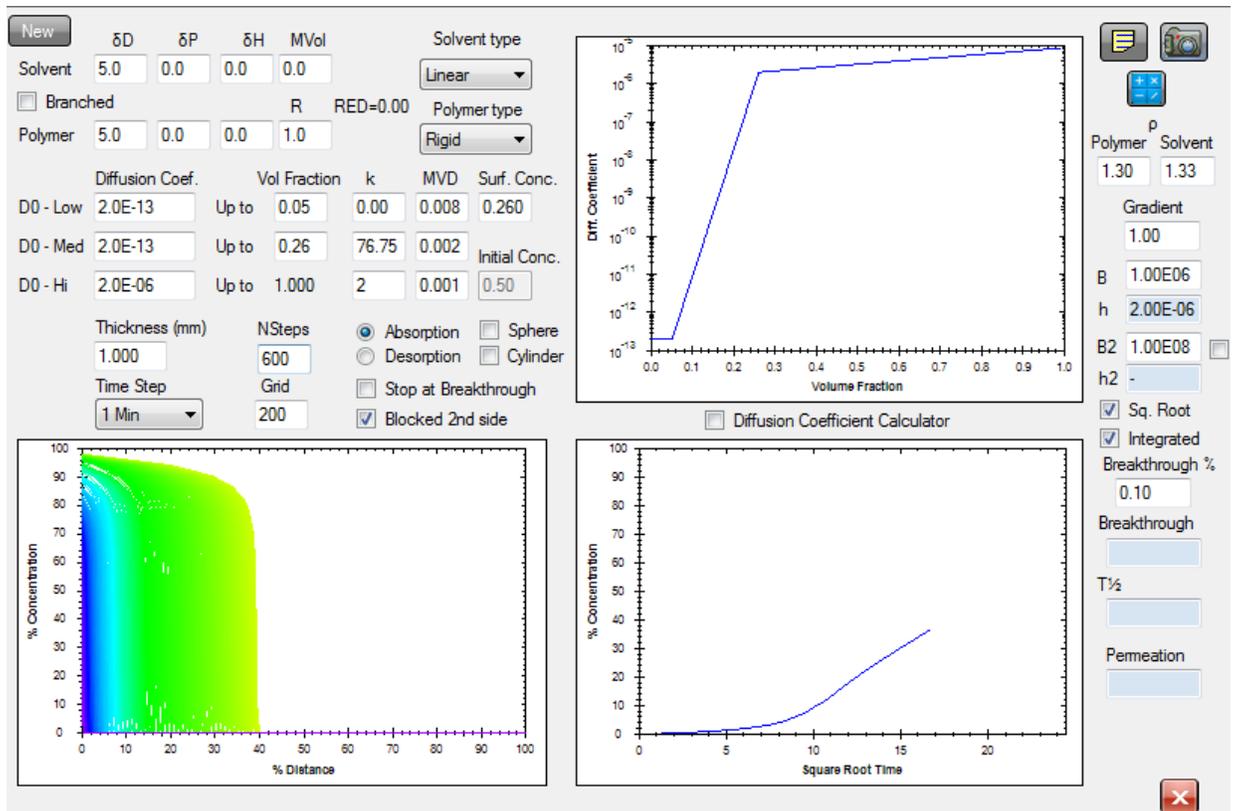


Figure 4 models the absorption of liquid dichloromethane into stretched and restricted cellulose acetate films as reported by Petropoulos and coworkers [24,25]. The precursor is modeled perfectly as is the absorption curve, but a straight line from the exposed surface at the highest concentrations leading to a step-like drop in the concentration gradient is not perfectly modeled. It is felt experimental factors lead to added solvent at the highest concentrations in the swelling film sandwiched between two microscope slides. The general features of the experiment are modeled rather well, however.

Similar equations have been used to model absorption in polymers by Petropoulos, his coworkers, and Hansen, respectively [1,26]. Curve fitting of absorption experimental results will therefore be similar and satisfactory to all of these. There are quite different interpretations for the parameters used, however. The “kinetic” stress relaxation modulus of Petropoulos and coworkers includes a rate parameter called β , which, in the relevant equations, is the counterpart of the surface mass transfer coefficient, h , used by Hansen.

7. Sigmoidal (two-stage) absorption involves a delay of the absorption at the start of an experiment. There appear to be (at least) three different situations that can provide this type of absorption curve. One of these is for the initial delay being caused by relatively low diffusion coefficients, for example in a dry film. As the concentration increases diffusion is faster in the plasticized film. The result is that the surface resistance becomes relatively more important. In cases for absorption to a viscous liquid state the process

resembles the drying of a lacquer film in reverse. A typical example of this is given in [19] where the data were analyzed with a bulk theory. These same data were found to fit a diffusion equation model in [6].

A second situation giving sigmoidal absorption is where the surface resistance retards absorption most at the start of the experiment. As absorption continues the diffusion resistance increases because of the requirement for diffusion further and further into the film. The diffusion resistance increases to such an extent that the surface concentration can slowly increase, reaching the maximum value at a rate depending on the balance between surface and (changing) diffusion resistance. This can happen for a constant diffusion coefficient, as modeled by Crank many years ago [27], as well as for a concentration dependent diffusion coefficient.

A third example of what has been called two-stage absorption is reported in [17] for absorption of supercritical carbon dioxide into a 1 micron thick film of PMMA. The experiments were interpreted with a bulk theory. These experiments were modeled with the diffusion equation confirming the surface resistance completely dominates the absorption process that takes 20-30 minutes for saturation of the samples [18]. The bulk model accounts for an effective diffusion coefficient that is about 4 decades lower than that expected for carbon dioxide in PMMA. The surface resistance control in this modeling using the diffusion equation allows the expected diffusion coefficient to prevail with a surface mass transfer coefficient that is reasonable (compare with the data in Figure 1, for example).

Some general comments follow:

Stress can hardly be a factor of significance in diffusion at concentrations giving a liquid system as has been assumed in many cases. It is also difficult to believe stress factors are major effects for elastomeric films. My own experience for poly(vinyl acetate) films is that absorption experiments above about 0.2 volume fraction of chlorobenzene all required consideration of the surface effects [5,6,23]. These films would be considered as being in an elastomeric region. Thicknesses were in the range of 100 microns and lower. Whether or not a surface effect is significant is also highly dependent on film thickness. Such effects are more important on a relative basis for thinner films.

The effects of film thickness changes with swelling by the solute in my modeling are fully accounted for by using the film divided into dry film intervals as reference. Crank did this as well [22]. If one wants the actual film thickness this must be found by including the volume of the solvent in the intervals used in the numerical method of solving the diffusion equation and then summing these volumes.

When measured diffusion or permeation coefficients change with film thickness one should look for a surface resistance. As film thickness decreases the surface effects become more significant relevant to diffusion in the bulk of the film.

It is recognized that results from the same systems in different laboratories will most likely be different because of different prior histories. Rates of cooling, production and annealing conditions, sample preparation, and retained solvent, among other things, can be expected to lead to differing results. This report emphasizes general phenomena and smaller differences are not expected to lead to any significant changes in the overall picture. A lot of work remains to fully confirm the diffusion equation methodology, but in the meantime guidelines are provided for improved understanding and product development. Relevant software is also available [20].

Conclusion

Explanations of “anomalous” diffusion based on the diffusion equation are compared with those based on stress relaxation, swelling stresses, or other bulk film properties. There are no “anomalies” since the diffusion equation solved properly can model what happens in all of the typical cases that were examined. Explanations based exclusively of bulk phenomena cannot satisfactorily explain these phenomena.

Solutions for the diffusion equation can be used in product development since these apply to all of absorption, desorption, and permeation. Diffusion coefficients measured correctly in one situation can be applied to another, and the effects of the different variables can be explored systematically. A powerful set of tools results when software solving the diffusion equation is coupled with software exploiting the Hansen solubility parameter concept. A mismatch of the Hansen solubility parameters for the polymer and the solute improves barrier properties by reducing the equilibrium uptake. This lowers concentration gradients, (exponential) diffusion coefficients, and entry mass transfer coefficients.

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