

Reinterpreting the Experiments of Carlà et al. for the Absorption of Supercritical Carbon Dioxide into PMMA

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Abstract

The absorption of supercritical carbon dioxide into PMMA was modeled by Carlà et al. in [1] using an approach that is 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 nonequilibrium thermodynamics in glassy polymers with references in [1] giving the details. The experiments in [1] are modeled here using the software available from www.hansen-solubility.com. The diffusion equation can be solved with a significant surface condition and exponential concentration dependence of the diffusion coefficients, if required. This modeling reproduces the results found in [1], showing that consideration of stress relaxation and related phenomena are not required to explain these experiments. The short-term bulk viscosity parameter, η^* , in the NET-GP approach apparently accomplishes the same as the surface mass transfer coefficient, h , in this modeling. In doing so it necessarily reduces the effective diffusion coefficient in the bulk of the polymer by about 4 orders of magnitude, from the expected average of $1(10)^{-7}$ cm²/s or slightly lower to near $5(10)^{-12}$ cm²/s. This would seem to require an explanation. This reduction in the effective diffusion coefficient is required since the time to reach equilibrium is 20-30 min for the 1 micron films. The surface concentrations as function of time in this modeling match those reported in the last figure of [1].

Introduction

The author was admonished in a review of a rejected manuscript as follows:

- It should be then accounted for the fact that variation in surface concentration (similar to those produced by "significant surface condition" model) can be also obtained through approaches which focus on bulk properties of penetrant-polymer mixture (similar to what it is done in "stress relaxation" model). For a similar approach see, for example, "Modeling Sorption Kinetics of Carbon Dioxide in Glassy Polymeric Films using the Nonequilibrium Thermodynamic Approach" Carlà et al., Industrial and Engineering Chemistry Research (2009), vol.48, pag. 3844, which deals with the description of a two stage sorption process, and see specifically the last figure in the paper for the representation of change in penetrant surface concentration.

This remark was strongly contributory to this author's decision to withdraw from reviewing scientific manuscripts other than for very special types and to acknowledge that an individual working without ready access to the relevant literature should perhaps even refrain from further activity of this kind altogether, including writing. There comes a time to withdraw. A complete response to the above is found in the following, however.

As an introduction to this response it will be mentioned that this same reviewer cited Thomas and Windle articles [2-8] as follows:

the author claims that representation of entry resistance, through model parameter h , can describe Case II kinetics for the case of penetrant sorption from pure liquid source. On the other hand, best known evidences of similar phenomena refer to Case II kinetics in which no appreciable change of the surface concentration is observed (see for example works by Thomas and Windle for sorption of liquid alcohols in PMMA published in Polymer in years 1978-82). It should be underlined in the paper that this is different from what embedded in the "significant surface condition" model, for which sorption order kinetics larger than 0.5 (anomalous, Case II or Super Case II) is invariably associated to convenient variation in time of surface concentration;

The answer to this is found in a download on www.hansen-solubility.com.

[Reinterpreting Case II Absorption in PMMA](#) An analysis of the Thomas and Windle data for the absorption of methanol into PMMA can be downloaded as a PDF document. This is confirmation that the diffusion equation can model these phenomena, without consideration of relaxation phenomena.

This document [9] uses the software in [10] to show that the step-like concentration gradients for methanol in PMMA reported by Thomas and Windle [2-8] are not representative of methanol. They are representative for iodine only in the methanol plasticized PMMA, since iodine was used as a tracer for methanol. This tracer is shown to be unsuitable since it significantly lags methanol. The surface concentration in Case II type diffusion is not constant in the experiments of Thomas and Windle as indicated in the above reviewer comment. The surface concentration of methanol increases with time and is very much dominated by a significant surface condition. It is again the combination of concentration dependent diffusion coefficients and a significant surface condition that are required to correctly model diffusion in polymers.

Results

In the following it will be shown that the software available from www.hansen-solubility.com is capable of modeling the results reported [1]. It should be noted that the film thickness used in [1] is nominally one micron with the film attached to a quartz microbalance to record weight changes. The carbon dioxide is in a supercritical state at 50°C, and the pressure is increased from one (high) value to another to increase the amount of carbon dioxide absorbed. There are some initial temperature changes that have required correction. This effect gives the impression of a two-stage process, but it is assumed that the two-stage curves referred to are the phenomena sometimes called S-shaped or sigmoidal absorption that are seen more clearly in Figure 6 in [1]. The absorption curves can be seen in Figures 1 and 2, taken from [1]. The absorption curve in Figure 1 is reproduced in Figure 3.

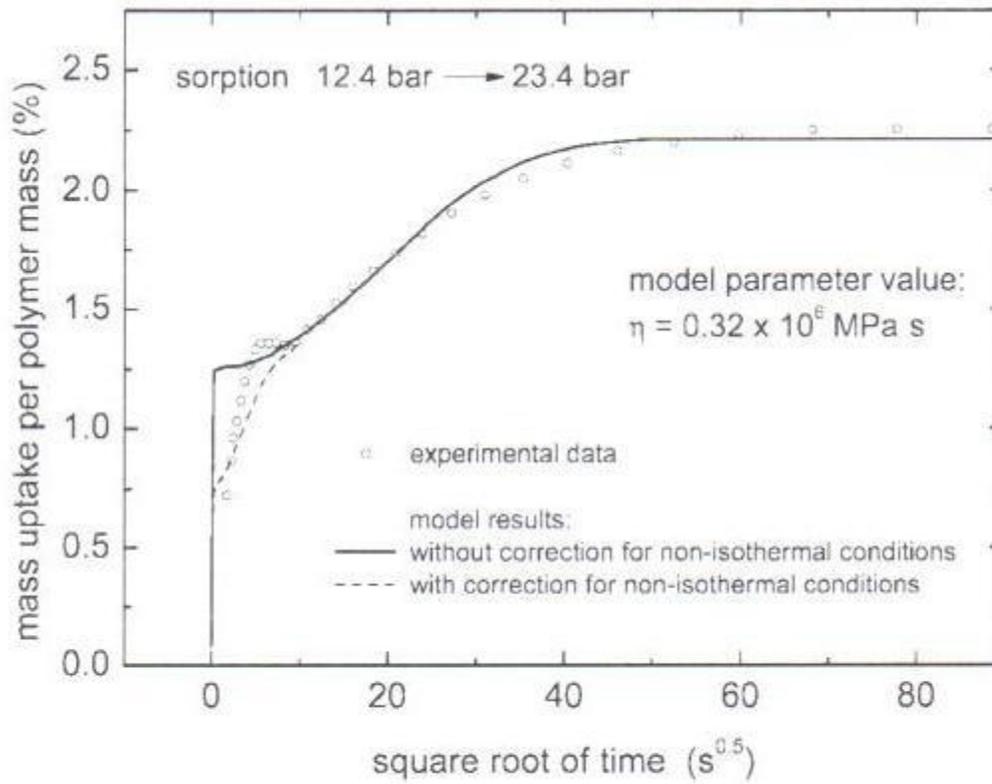


Figure 5. Kinetics of CO₂ sorption in a PMMA film for a sorption step from 12.4 to 23.4 bar. Comparison of experimental values with model results.

Figure 1. The absorption of carbon dioxide into a thin film of PMMA given in Figure 5 in [1].

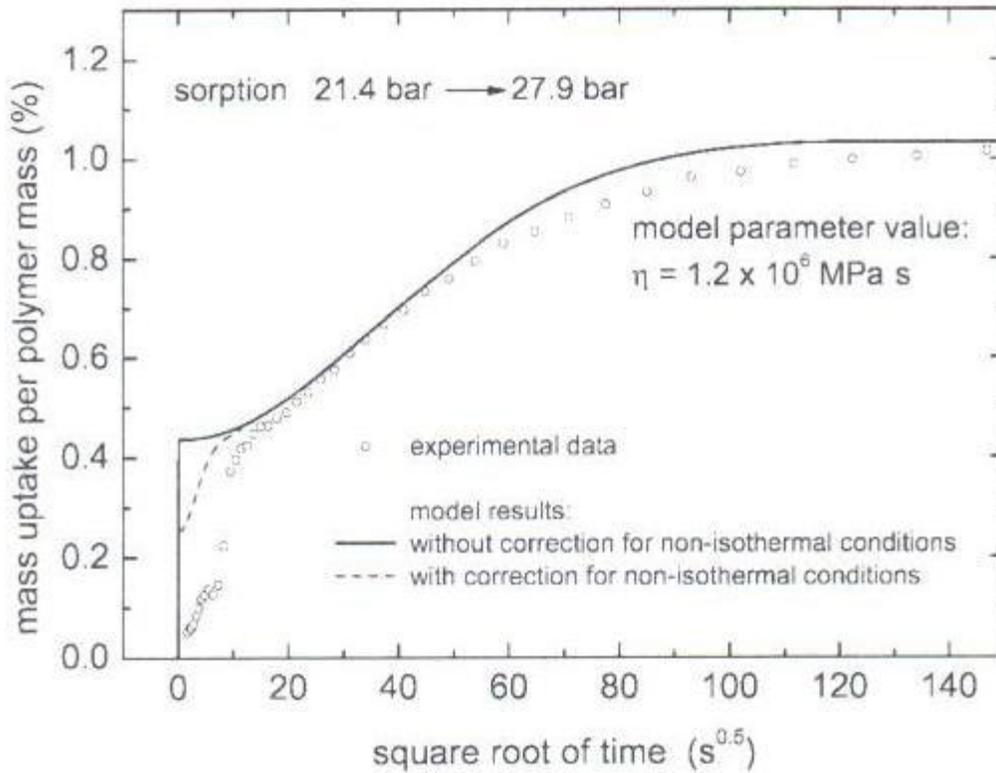


Figure 6. Kinetics of CO₂ sorption in a PMMA film for a sorption step from 25.4 to 33.1 bar. Comparison of experimental values with model results.

Figure 2. The absorption of carbon dioxide into a thin film of PMMA [1] given in Figure 6 in [1].

The diffusion modeler included in [10] was used to model the general results in Figures 1 and 2[1]. Figure 3 gives a representative result that matches the behavior reported in Figure 1 [1]. The results of Figure 2 could also be reproduced by a small decrease in the h parameter. The initial uptake and curvature is masked by the heat effects, but once these become less significant, the modeled uptake curve matches the experimental results.

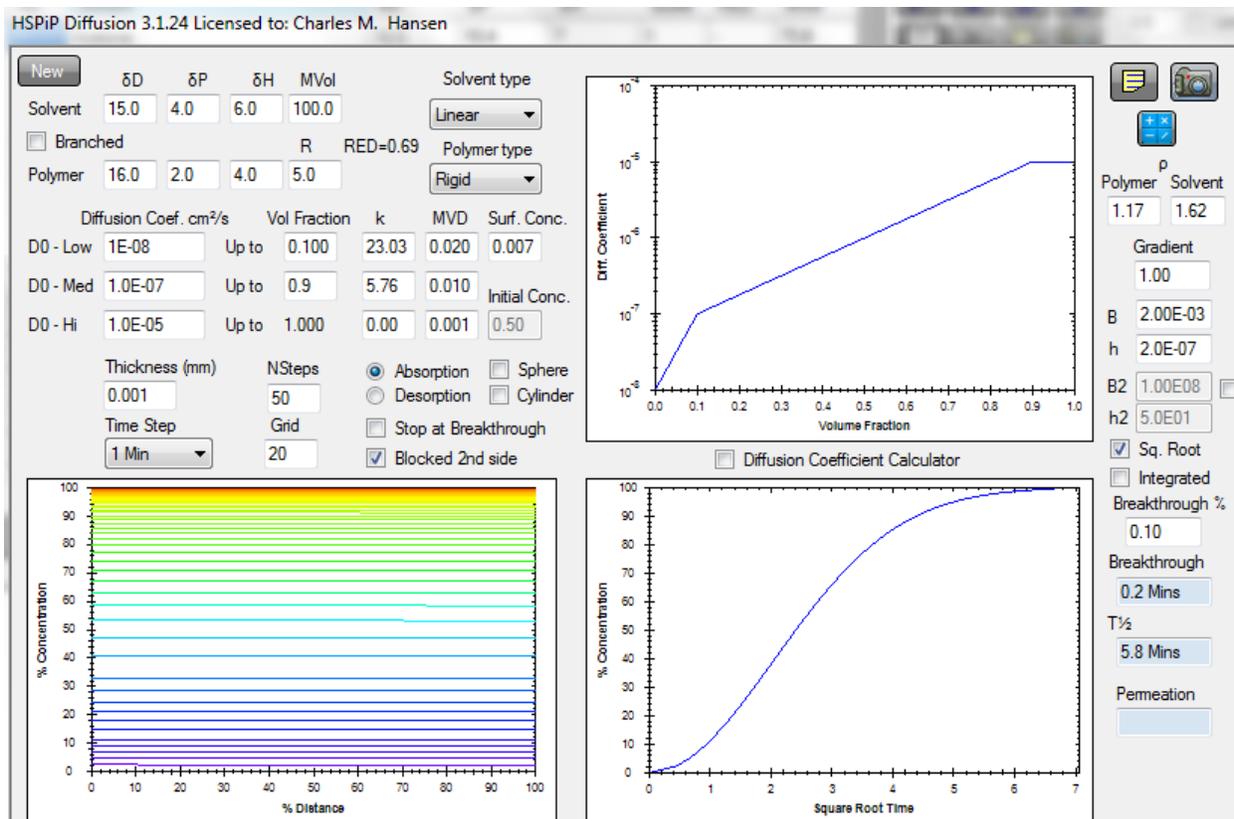


Figure 3. Modeling the uptake of supercritical carbon dioxide into a 1 micron thick film of PMMA on a quartz microbalance.

The concentration at equilibrium uptake in this example is only about 0.007% by volume, so the diffusion coefficients at concentrations above this shown at the upper right are not used to model the experiment but are supplied to satisfy the requirements of the software. D_0 could be considered as a constant. D_0 is taken here as $1(10)^{-8}$ cm^2/s , but essentially the same result would be obtained for values as low as $1(10)^{-11}$ cm^2/s . The density for the supercritical carbon dioxide was taken from [1] as $\rho^*=1.62$ g/cm^3 , but widely different values are not critical in this interpretation of the experiment. There is an S-shaped, sigmoidal, or if you will “two-stage” uptake curve at the lower right. The surface condition controls the uptake essentially from the start as can be seen by the flat concentration gradients shown at the lower left. These data match Figure 4 of [1] reproduced as Figure 1 in this document shortly after the initial period except that (minutes)^{0.5} are used here rather than (seconds)^{0.5}.

The uptake is completely determined by the h value that is taken as $2(10)^{-7}$ cm/s in Figure 3. Almost any D above about $1(10)^{-11}$ cm^2/s will not affect the result shown in the figure in any significant manner. The diffusion coefficient must be in the range of $1(10)^{-12}$ cm^2/s to $6(10)^{-12}$ cm^2/s to have any influence on the absorption phenomena in the experiments reported in [1]. This was confirmed by the modeler as well as estimating the time for saturation of a 1 micron film using the relation D_0t/l^2 equal to about 1. When the diffusion coefficient is constant the

uptake will be about 95% of the equilibrium at this condition [11]. This range of diffusion coefficients is about 4 orders of magnitude lower than that assumed as being reasonable for the experiments. It should be noted, however, that the time to reach equilibrium uptake in these 1 micron films is about 25-30 minutes. The NET-GP approach models these relatively long times by adjusting the short term polymer viscosity. In other words the effect of the (local?) stress within the film must reduce the (local?) diffusion coefficient by about 4 orders of magnitude relative to $1(10)^{-7} \text{ cm}^2/\text{s}$ that might be thought reasonable in order for the uptake curve to be only very approximately matched. This appears to be a situation that requires further explanation.

Figure 4 is taken from [1] where it is the last figure (Figure 8). This is the figure referred to by reviewer number 2 in the above as requiring comment. The surface concentration is given as a function of the time.

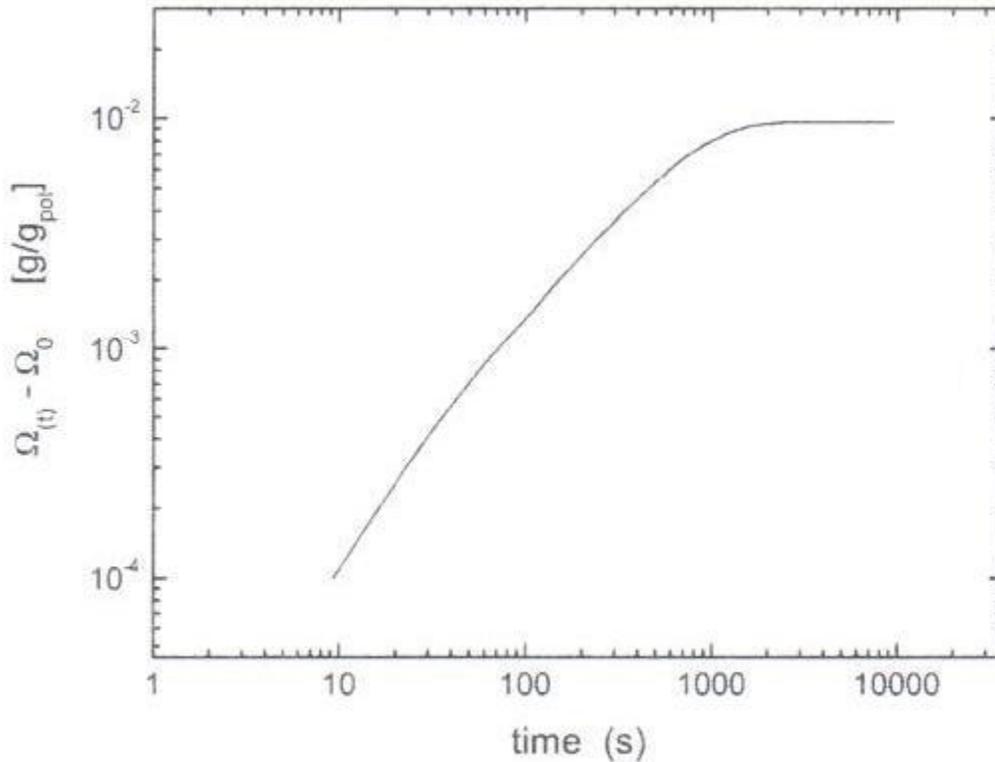


Figure 8. Model results for the kinetics of CO₂ mass ratio increase in PMMA at the film interface for a sorption step from 12.4 to 23.4 bar.

Figure 4. Surface concentration of carbon dioxide in the PMMA film for the conditions given in the figure. Note that the concentration in the uptake curve reported in Figure 5 at the lower right

also gives the surface concentration since there are no concentration gradients in the film. The concentrations in Figure 4 are found in Figure 5 for the same elapsed times.

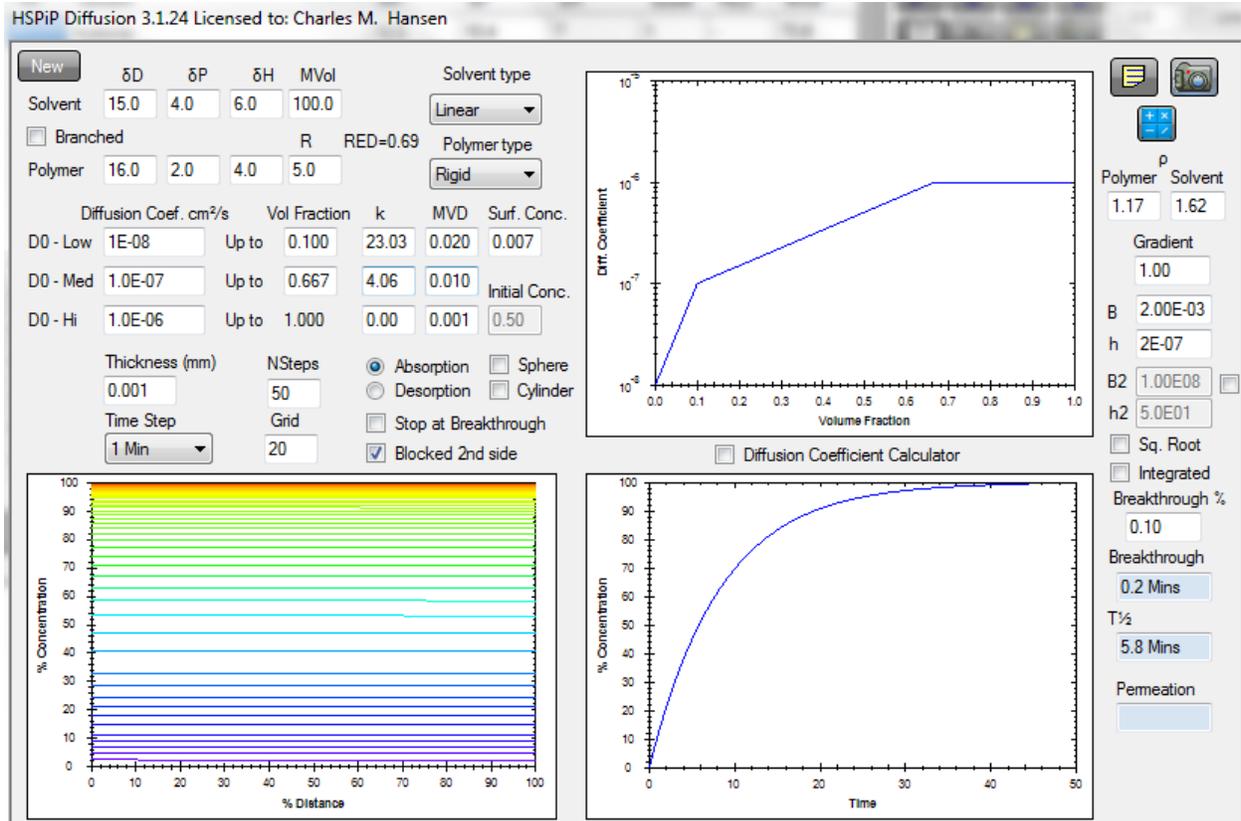


Figure 5. The same data are used in Figure 5 as are used in Figures 1 and 3. The uptake curve at the lower right is now plotted using linear time rather than using the square root of time. This was done to more easily read concentrations from the computer screen. The concentrations in the curve at the lower right are surface concentrations as well as bulk concentrations as can be seen from the flat concentration gradients at the lower left. These surface concentrations match those modeled in [1] in Figure 8 that is reproduced here as Figure 4. It is these that the reviewer cited above wished to see referenced to show that bulk properties could also be used to produce surface concentrations that increase with time.

Discussion

Figures 1 through 5 confirm that the modeling done in this document matches the experimental data and modeling done in [1] within reasonable limits. Both the NET-GP approach and that presented here appear to do satisfactory modeling of the experimental data. There is a dilemma as to which approach is the correct one.

It has been shown that the methodology presented here using solutions to the diffusion equation with an exponential dependence on concentration and with a potentially significant surface

condition suitably explain the experiments of Thomas and Windle [2-8], Petropoulos and coworkers [12,13], anomalous absorption in polymers in general [14], and the here the experiments of Carlà et.al. [1]. It was pointed out in a manuscript rejected by the European Polymer Journal (where the reviewer involved in this report was reviewer number 2) that the h used in the methodology in [14] and here is completely analogous to the rate parameter used by Petropoulos and coworkers called β . The summary of this rejected manuscript is/was as follows:

“Similar equations have been used to model absorption in polymers by Petropoulos, his coworkers, and Hansen, respectively. 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. Both enter respective dimensionless quantities in models for absorption based on (numerical) solutions to the diffusion equation. A stress relaxation interpretation seems improbable for absorption of vapors to high solvent concentrations. The diffusion coefficient is high enough to assure an essentially uniform concentration gradient and very mobile polymer chains. A significant surface mass transfer coefficient in vapor absorption reflects transfer of the latent heat of condensation away from the film, diffusion in air above the film, etc. A kinetic stress relaxation model for desorption or steady state permeation is not possible. All of these have been modeled satisfactorily using verifiable and consistent parameters by Hansen. This latter approach includes exponential diffusion coefficients as predicted by free volume theory. A surface entry mass transfer coefficient that can approach zero may also prevail when larger and/or more bulky molecules have difficulty entering and passing through the polymer surface, even though they may be there in abundance. It is such cases that clearly yield what are called Case II and Super Case II absorption curves and concentration gradients have advancing fronts. A very special case of dichloromethane absorption into simultaneously restrained and stretched cellulose acetate is modeled perfectly here in the direction across that of stretching using concentration dependent diffusion coefficients with no significant mass transfer coefficient. A different physical model is thought necessary for diffusion in the direction of orientation. This is based on the slow “freeing” of the highly associated, long, stiff polymer molecules allowing very rapid diffusion behind the front and very slow diffusion in its precursor. This physical model is supported by calculations using relevant parameters, with stress relaxation considerations not being required.”

The analysis of the Thomas and Windle experiments for the absorption of methanol into PMMA is given in [9]. The step-like concentration gradient is described as misleading. The iodine used as tracer is not suitable since it lags the methanol, and gives a false indication of a step-like concentration profile. The methanol concentration gradients modeled by the software in [10]

meet at the center of a free film much sooner than those of iodine, the latter giving the appearance of a step-like profile prior to reaching the middle of the free film.

Table 1 gives the approximate surface mass transfer coefficients reported in [9] for absorption of methanol into PMMA as found by analysis of the data of Thomas and Windle [2-8].

Table 1 Approximate entry mass transfer coefficients for methanol in PMMA with temperature and equilibrium uptakes.

h, cm/s	Temp. °C	Equilibrium concentration, vol. fract.
1.4E-05	62	0.42
1.1E-06	30	0.26
4.1E-09	0	0.24

The approximate entry mass transfer coefficient for the carbon dioxide experiments examined here is $2(10)^{-7}$ cm/s. This does not seem unreasonable in view of the data in Table 1 and the very low uptake. Low equilibrium uptake could influence the adsorption and subsequent absorption. Low equilibrium uptake could also be an indication of exceptional difficulty in adsorption, finding a suitable entry site, and finally absorbing into the bulk, all of which influence the magnitude of h.

Examples of successful modeling of “anomalous” diffusion including S-shaped, Case II and Super Case II absorption in polymers are given in [14] as further evidence for the capabilities of this approach.

The nonequilibrium thermodynamics of glassy polymers (NET-GP) approach was used in [1] with apparent success. In addition to all of the arguments in the above related to the incorrect interpretation of diffusion in polymers based on relaxation phenomena, one must consider the following points that have become evident in [1].

The rate of uptake clearly slows toward the last of the experiments to a very low value in spite of the fact that the concentration of plasticizing carbon dioxide is near its equilibrium value. It is to be expected that plasticizing increases diffusion rates because of the added free volume in the system. In addition the rate of any stress relaxation should increase with increased free volume. This is clearly explained by a significant surface condition where the driving force for uptake at the surface decreases with time and becomes very small at the last asymptotic stages as equilibrium is approached. This behavior is also seen in Case II and more clearly in Super Case II experiments. How does the NET-GP (or other approach) account for the asymptotic approach

to equilibrium at very long times that is frequently found in absorption experiments characterized by Case II or Super Case II, as well as in the experiments reported in [1]?

In the absence of a significant surface condition the prevailing diffusion coefficient in that part of the film where diffusion is controlled must be in the range of $1(10)^{-12}$ cm²/s to $6(10)^{-12}$ cm²/s (or perhaps lower) to have any influence on the absorption phenomena in the experiments reported in [1]. Otherwise the absorption curves would not be as they are, taking substantially long times to reach equilibrium. How does one explain such a low local diffusion coefficient in the bulk of the polymer? It is about 4 orders of magnitude lower than that assumed in [1] for the diffusion coefficient of carbon dioxide in PMMA, $1(10)^{-7}$ cm²/s, under the given conditions.

It has become obvious that a key parameter used in [1], η^* , described as “a model parameter for the short-term bulk viscosity in the glassy polymer system” is related in function to the surface mass transfer coefficient, h , used in this manuscript. There are a host of other parameters in the NET-GP approach, in contrast to the present use of the diffusion equation, exponential (or constant in this case) diffusion coefficients, and a surface/entry mass transfer coefficient, where required. The η^* used in [1] must be closely related to the β used by Petropoulos and coworkers.

Conclusion

The experiments of Carlà et.al. [1] have been satisfactorily modeled using the diffusion equation and a significant surface mass transfer coefficient. There was no need to consider stress relaxation phenomena or similar concepts. . The surface concentrations as a function time in this modeling match those reported in the last figure of [1]. This follows satisfactory modeling all forms of absorption commonly called “anomalous” [14], the stretched, constrained film experiments of Petropoulos and coworkers [12,13], and the “Case II” experiments of Thomas and Windle [2-8].

This author is not motivated by the results of [1] to change his opinions as to the origins of these phenomena. There is no need to invoke stress relaxation, viscous polymer behavior, or similar phenomena to understand absorption into polymers. There are indeed stresses, but their effects are apparently not as significant as has been thought. One need not consider them specifically as the simple modeling presented here has shown.

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Charles M. Hansen, July, 2012

Editorially revised in connection with a manuscript, October, 2012