

A Different Interpretation of the Hedenqvist and Gedde (Polymer 1999) Study for n-Hexane Diffusion in Natural Rubber and Low Density Polyethylene

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Abstract

The absorption and desorption of n-hexane in natural rubber (NR) and a low density polyethylene (LDPE) were studied and modeled by Hedenqvist and Gedde with an interpretation based on surface swelling stresses. This interpretation is shown to be unnecessary and additionally is judged to be incorrect. The diffusion equation with a significant surface condition and exponential diffusion coefficients can satisfactorily model the experiments. A comparison of different approaches to model S-shaped absorption curves is given. The diffusion equation itself can apparently handle what is often called “time-dependent” phenomena.

Introduction

A statement questioning my lack of incorporation of stress related effects was made from the audience at the end of my presentation at the 50th Nordic Polymer Days in Helsinki on May 30, 2013 [1]. While I said I did not intend to analyze the data in the article cited below, this is a brief analysis of the background for the comment (and rejection of a manuscript) anyway. The article in question is [2]:

Hedenqvist MS, Gedde UW. Parameters affecting the determination of transport kinetics data in highly swelling polymers above T_g . *Polymer* 1999;40:2381-2393.

The absorption and desorption of n-hexane in natural rubber (NR) and a low density polyethylene (LDPE) were studied and modeled with an interpretation based on surface swelling stresses. The purpose of this report is to demonstrate that surface swelling stresses are not necessary to satisfactorily model the experiments. It is demonstrated that the diffusion equation solved with exponential diffusion coefficients, $D(c)$, and a potentially significant surface mass transfer coefficient, h , can do this. The usual assumption of an immediate change of the surface concentration to the equilibrium value is valid only when h is sufficiently high. A significant surface condition most often leads to an exponential increase in the surface concentration on absorption, depending on when it begins to be significant in the experiment relative to the diffusion resistance at the surface and in the bulk. The diffusion coefficients are referred to dry polymer thus eliminating any concerns about swelling effects and changing film thickness. The distance plots in the figures below are therefore based on dry polymer. If one wishes the actual film thickness the increase in the volume of each element in the numerical analysis because of solute must be added to the dry film volume. A comparative discussion of different approaches to account for S-shaped absorption curves is given in the following.

Method

Data were read as accurately as possible from given figures in [2]. These data were then entered into a diffusion modeler [3]. The figures below are screen shots of results that model the experimental data satisfactorily. Data were read from the figures in [2] at given lapsed times, such as 20%, 50%, 90%, etc. change in the mass content. One can read the results on the computer screen for any point on any curve in the modeling for comparison. This modeling involves iteration of the input estimates for the mass transfer coefficient, h , and the diffusion coefficients until the solutions satisfactorily model the experimental data. The resulting values all seem believable. The screen shots for the figures below were made when the modeling satisfactorily matched the experimental data.

Results

Screen shots from the HSPiP software [3] are given in the following for the absorption and desorption of n-hexane into and from NR and LDPE, resp.

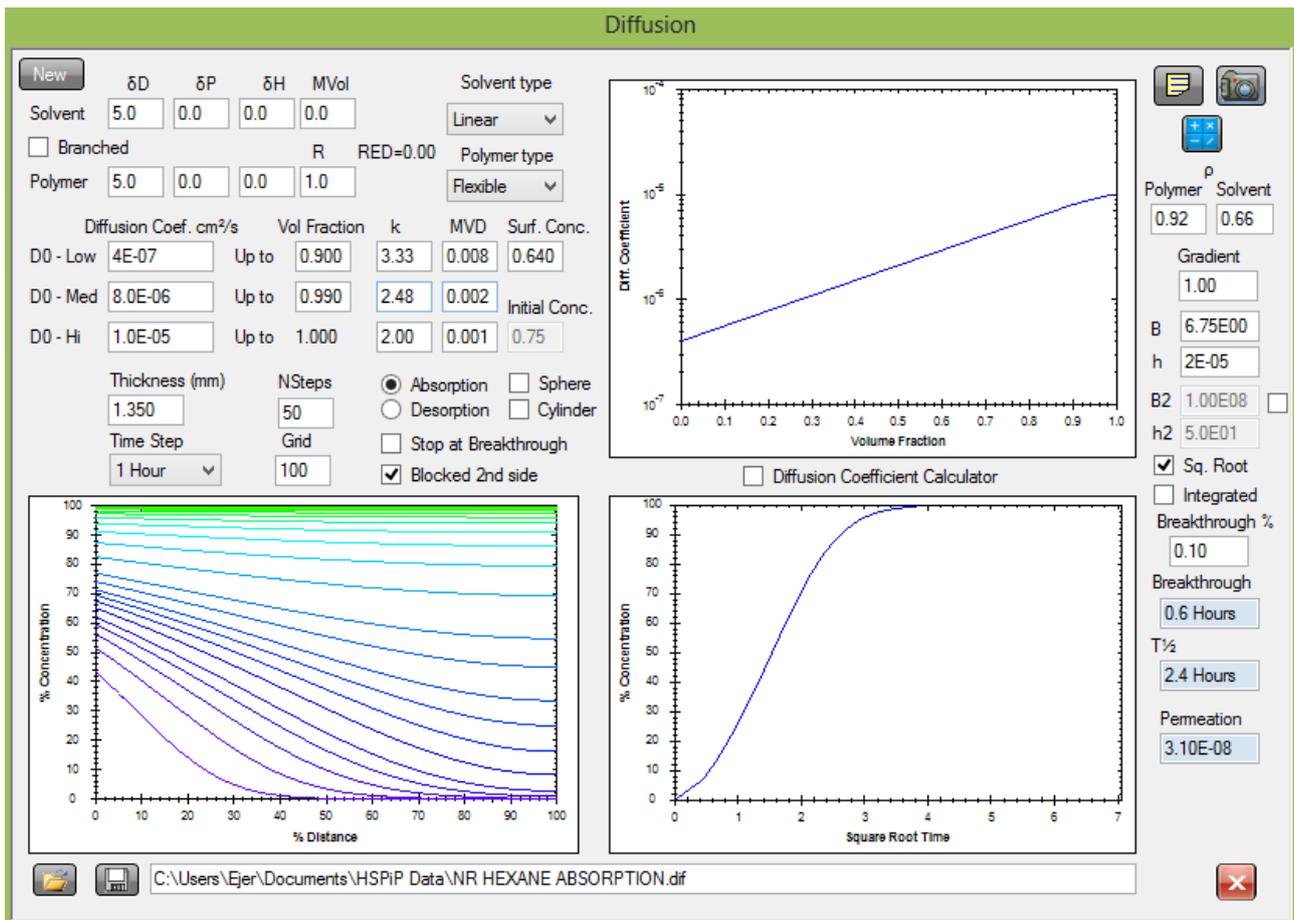


Figure 1. Modeling of the absorption of n-hexane into natural rubber upon liquid contact.

Figure 1 models the absorption of n-hexane into natural rubber samples based on the data in Figure 4 in [2]. The diffusion coefficients assumed are given graphically at the upper right in the figure and in the entries at the upper left. The diffusion coefficient increases from $4(10)^{-7}$ cm²/s (D_0) at zero concentration to $3.4(10)^{-6}$ cm²/s at the equilibrium amount (0.64 volume fraction). Data for concentrations higher than 0.64 volume fraction are not used. There is a significant surface condition as shown by the slow increase of the surface concentration to the equilibrium value as can be seen in Figure 1 at the lower left. The concentration gradients are rather flat and certainly nothing that approaches an advancing front. These concentration gradients differ from those in Figure 8 in [2] that model the same experiment, since all of the curves for different elapsed time appear to originate at the surface at the equilibrium concentration. This is because the model used produces a straight line on a square root of time plot as can be seen in Figure 7 of [2]. The experimental S-curvature is not reproduced. Since the measured uptake curve does have the S-curvature, it would appear that the modeling in Figure 1 is to be preferred over the modeling reported in Figures 7 and 8 in [2]. The uptake curve at the lower right matches the experimental data well with check points at relative concentrations of 0.5 and 0.965. The S-curvature in the uptake curve is the result of a significant surface condition. The surface mass transfer coefficient, h , given in the middle on the right in the figures, is found to be $2(10)^{-5}$ cm/s in this case.

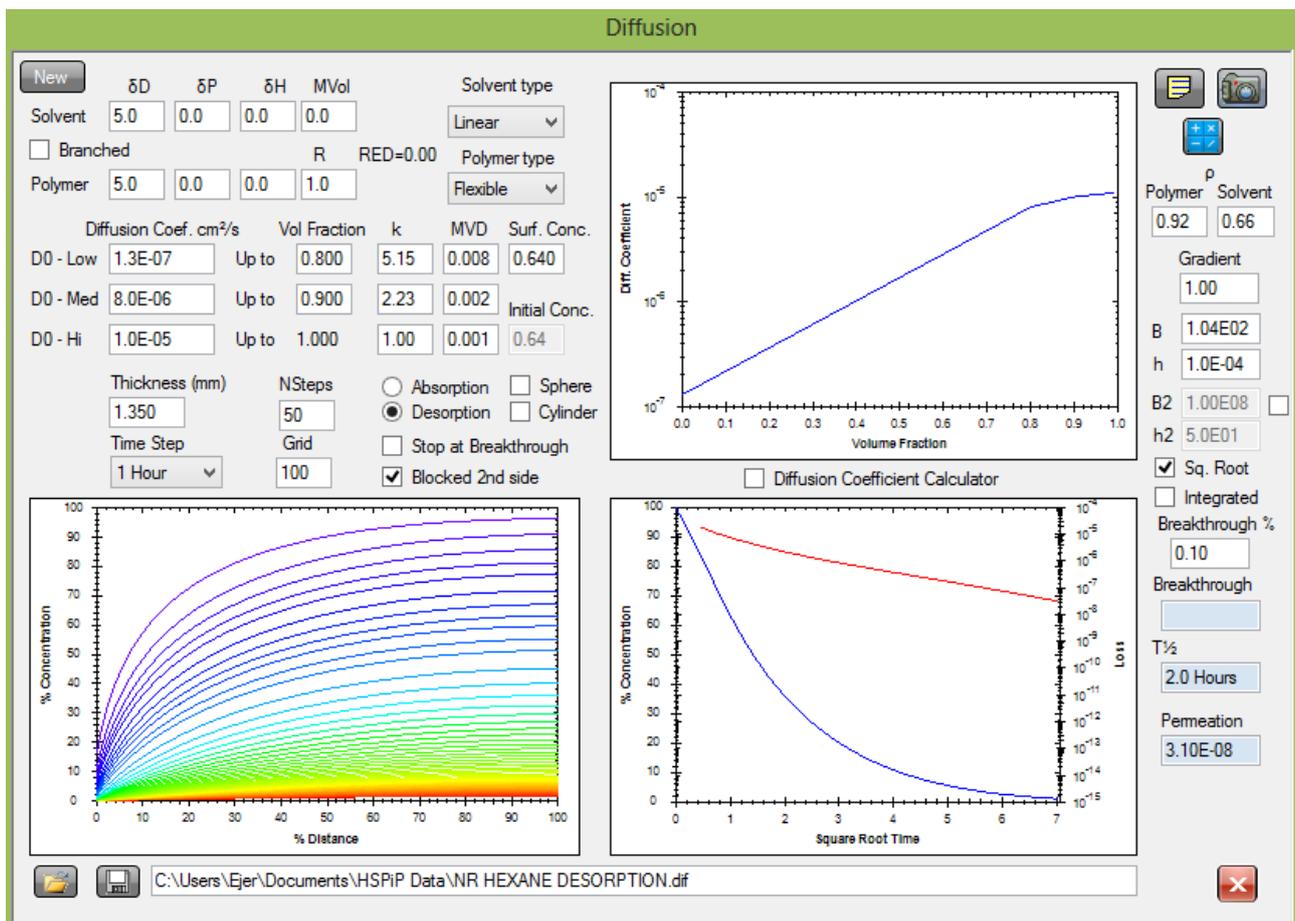


Figure 2. Modeling of desorption of n-hexane from saturated natural rubber into air.

Figure 2 models desorption to air of n-hexane from natural rubber samples based on the data in Figure 5 in [2]. The diffusion coefficients are given graphically at the upper right and numerically in the entries at the upper left. These diffusion coefficients are not identical with those used in Figure 1. D_0 is $1.3(10)^{-7}$ cm^2/s and D at the equilibrium amount is $3.5(10)^{-6}$ cm^2/s . These values are lower than those used for absorption, probably because of loss of plasticizing, lower molecular weight material from the polymer during the absorption experiment. The surface mass transfer coefficient was arbitrarily chosen not to have any effect. The surface concentration falls immediately to zero at the start of the experiment as assumed in [2]. The blue curve at the lower right gives the relative amount of mass remaining while the red curve gives the prevailing rate of loss of mass.

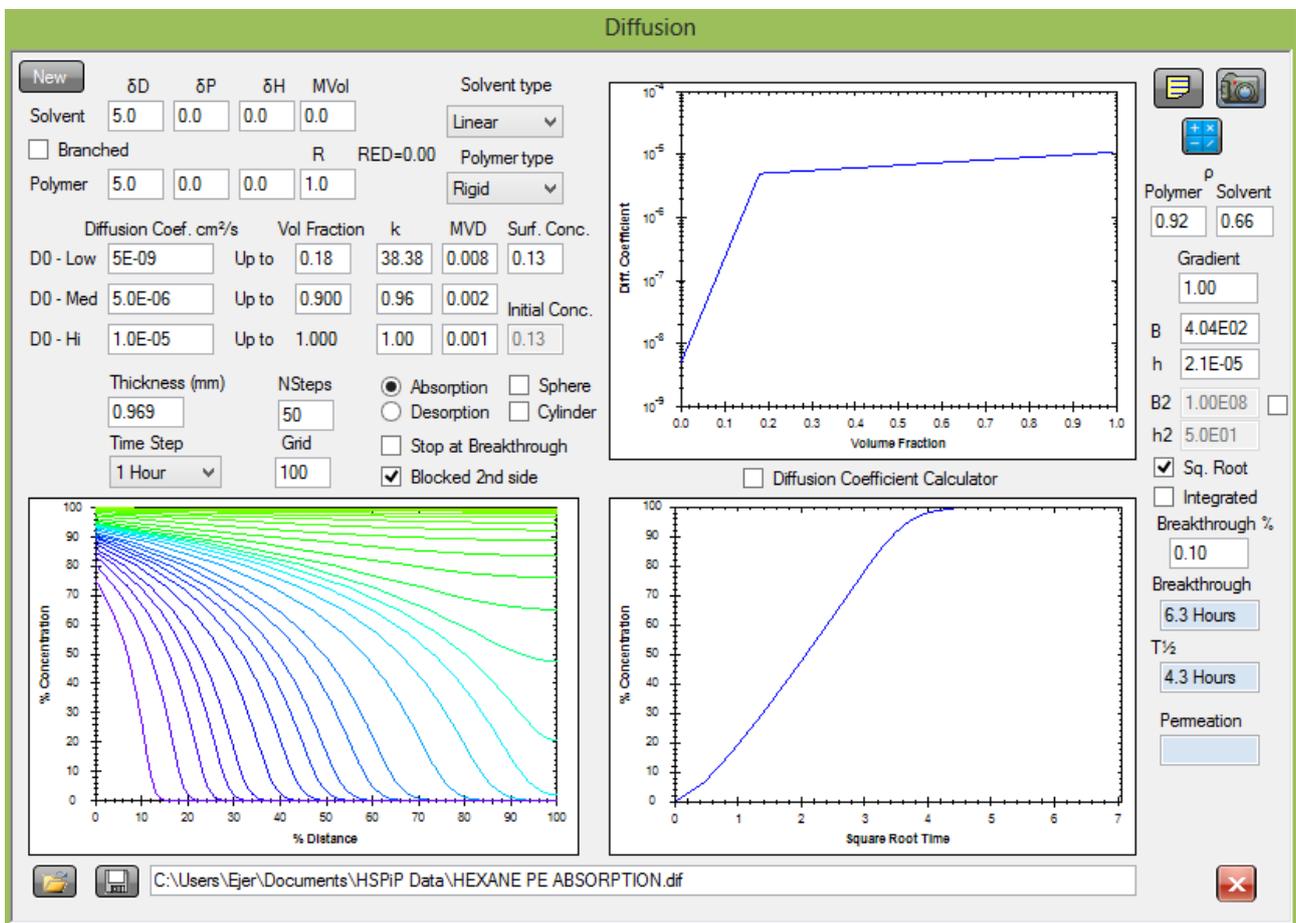


Figure 3. Modeling the absorption of n-hexane into LDPE upon liquid contact.

Figure 3 models the absorption of n-hexane into LDPE based on the data in Figure 10 in [2]. The diffusion coefficients assumed are given in the figure at the upper right and in the entries at the upper left. The experimental absorption curve is matched very well. D_0 is $5(10)^{-9}$ cm^2/s with D at the equilibrium value (0.13 volume fraction) being $7.3(10)^{-7}$ cm^2/s . The concentration gradients relative to the saturation value at the lower left show there is some effect from the surface condition, this being the cause of the S-curvature in the uptake curve at the lower right. The surface

concentration does not immediately rise to the equilibrium value. The surface mass transfer coefficient used was $2.1(10)^{-5}$ cm/s, which is essentially equal to that used in the Figure 1.

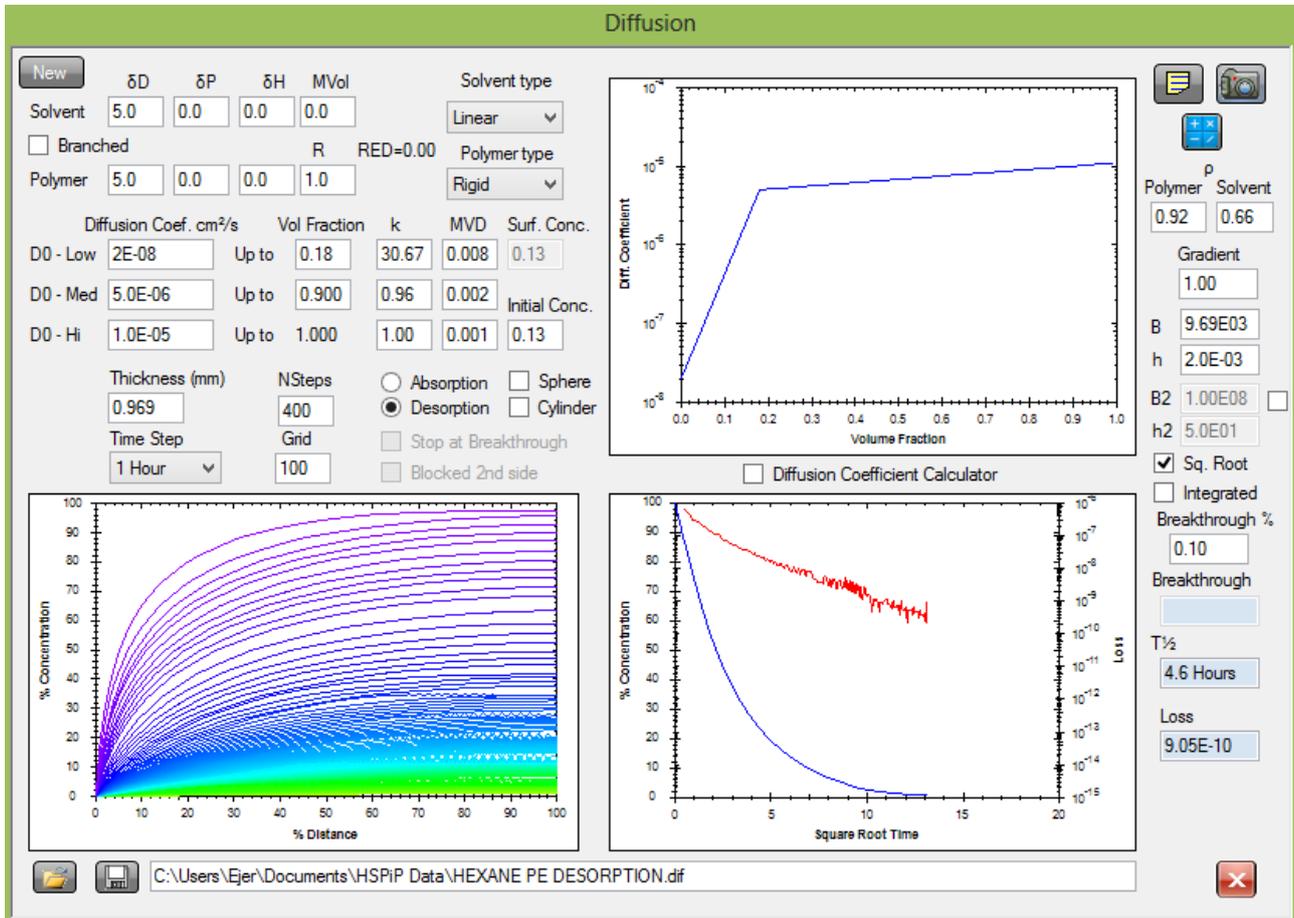


Figure 4. Modeling of desorption of n-hexane from saturated LDPE into air.

Figure 4 models desorption of n-hexane from LDPE with data based on Figure 24 in [2]. The assumed diffusion coefficients are given graphically in the upper right figure and in the entries at the upper left. D_0 is $2(10)^{-8}$ cm²/s and D at the equilibrium concentration is $1.1(10)^{-6}$ cm²/s. These values are higher than those found in absorption, presumably because the morphology within the LDPE has changed (opened) at the high solvent content. The concentration gradients are given at the lower left on a relative basis. There is no significant surface condition for this experiment as confirmed by reading on the screen for the uppermost (first) curve in the figure at the surface. The loss curve given in blue at the lower right satisfactorily reproduces the experimental data. The red curve is for the instantaneous rate of loss and becomes a little unstable at very low values. The assumed diffusion coefficients represent the experimental data very well. The surface mass transfer coefficient has been set high enough to not be significant, so it is not relevant to compare it with data in the figures above.

Discussion

The modeling in Figure 1 confirms that the surface condition is significant for absorption of n-hexane in the natural rubber experiments. The equilibrium concentration was 0.64 volume fraction at the end of absorption and the start of desorption. In the literature for chemical protective gloves this system is noted for giving degradation and very short breakthrough times [4]. For the LDPE there is a moderately significant surface mass transfer coefficient on absorption to 0.13 volume fraction n-hexane. This is presumably because n-hexane has some trouble orienting suitably in the direction allowing easiest entry, but surface morphology is certainly also important. There are also a limited number of entry sites available in the LDPE surface based on the relatively low equilibrium solubility with liquid contact. The surface condition is not significant for desorption of n-hexane from this equilibrium amount in the LDPE samples.

It is stated in [2] that the cross-sectional area of the samples decreased more rapidly than specimen thickness in both systems. Quote: “This may be explained by the homogeneous solute concentration distribution during desorption compared with the steep gradients prevailing during sorption.” In the first place there are no steep gradients during sorption as can be seen in Figures 1 and 3. Secondly, I would rather have read that edge effects are significant and that the unaccounted for additional loss from the edges would enhance changes in dimensions in the plane of the samples relative to the direction of desorption. The thickness of the NR samples is listed as 2.715 – 3.46 mm in the text (but what is used in the figures is not given). For edges 32.6 mm square, the initial slope for absorption/desorption for a constant diffusion coefficient will be higher than in the absence of edge effects by a factor of 1.36 – 1.47 (for the minimum and maximum thicknesses given above). This should certainly enhance changes in length and width dimensions in the films relative to their thicknesses. The equation used for this calculation is found in [5,6] where it is used to correct apparent diffusion coefficients based on the initial slope method:

Equation 1
$$D_0 = D_{app}/(1 + L/w + L/l)^2$$

D_0 is the true diffusion coefficient, D_{app} is the diffusion coefficient that would have been calculated in the absence of this correction, L is the film thickness, w is the sample width, and l is the sample length.

The diffusion coefficients modeling the NR experiments are higher for absorption than for desorption, presumably since some plasticizing material has been removed during the absorption experiment. In contrast to this the LDPE has higher diffusion coefficients after the absorption experiment, presumably because the morphology within the polymer is changed by the strong swelling at maximum uptake. There is a significant surface boundary condition in both absorption experiments, while desorption in both cases occurs with an immediate change of the surface concentration to zero.

It is recognized that the modeling here might be perfected by further adjustment of the variables, but this is not considered necessary under the circumstances. There is good agreement in the present version with variation being introduced by errors in reading from the curves in the journal article,

uncertain film thicknesses for the natural rubber samples, edge effects, and the probable degradation of the natural rubber samples (2 percent weight loss in the absorption experiments with possible effects in the remainder of the polymer), etc. It has been shown that a significant surface condition combined with estimated, exponential diffusion coefficients allows the diffusion equation to model the experiments in [2] without any need to mention stress relaxation, surface swelling stresses, special time related effects, or the like.

A Comparison of Approaches

The boundary condition in one dimension, x , used here is:

$$\text{Equation 2} \quad F_s = -D_s \partial C_s / \partial x = h(C^{eq} - C_s)$$

F_s is the mass flux passing through the surface at any time in g/cm^2s . There are two resistances in series to this flux. One is on the polymer side and one is on the external phase side. Either one may dominate or be negligible in given situations, but both are many times having an effect at the same time. D_s is the diffusion coefficient on the polymer side at the surface with the units cm^2/s . C_s is the surface concentration and C^{eq} is the final, uniform concentration in the experiment. It is emphasized that the units of concentration used here are $g \text{ solvent}/cm^3$ of dry polymer. The mass transfer coefficient is given in cm/s . It has been considered constant in all of my work. This seems to work well, perhaps because the polymer chain segments at the surface continually orient toward the external phase in the same way whenever possible to reduce the free energy at the surface to as low a value as possible.

It should be noted that the equation used in [2] to model stress effects is very similar to that used for the surface boundary condition in the current modeling [3]. In [2] the key parameter is called a surface concentration relaxation time with units of time while this author calls the key parameter the surface mass transfer coefficient, h with units of cm/s as noted above. There is no additional direct time effect introduced with the present procedure; time effects are handled by the diffusion equation itself.

Equation 3 is used in [2] in conjunction with the following statement:

“The stress build up in the plate during extensive swelling may lead to a time-dependent surface concentration [19], [21]. The concentration is therefore described by:

$$\text{Equation 3} \quad \tau_s \partial C / \partial t + (C - C^{eq}) = 0$$

....and τ_s is the surface concentration relaxation time.”

The discussion in [2] then proceeds to stress effects on dimensional changes. It is my contention that time effects are already included within the derivation of the diffusion equation. This means add-on terms to artificially produce an advancing front or terms related to stress/time considerations are not appropriate.

Equation 3 is the same as that used by Petropoulos and coworkers [7 and references therein] with τ_s being equal to β^{-1} :

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

Relevant experiments reported by Petropoulos and coworkers have also been analyzed and found to be fully explained by the diffusion equation with a significant surface condition and exponential diffusion coefficients [8,9].

As pointed out in [8], β could be replaced by h/L or the reverse, h could be replaced by β (adjusted by the film thickness) and the calculated results will be very close. The interpretation is then up to the individual as to which mechanism is the correct one since each of these equations can produce absorption curves that can be indistinguishable from each other. This is particularly true when the surface condition does indeed strongly influence or control the absorption process since the surface concentration will then, respectively, be close to or equal to the concentration throughout the bulk of the film for all practical purposes.

There is no need to mention a step-like advancing front in the absorption experiments. The step-like advancing front reported by Petropoulos and coworkers [7] is the result of leakage of some kind due to incomplete sealing of an oriented cellulose acetate film sandwiched between two glass microscope plates. The absorption of the liquid dichloromethane in the direction of orientation takes place much faster than any diffusion process could fully account for. The diffusion coefficient(s) required to establish this “front” and give the very high and flat concentration profile at high solvent content would have to be several times larger than the liquid self-diffusion coefficient of the dichloromethane solute. This is clearly impossible and eliminates this as an example of a step-like, advancing front for absorption into polymers. The step-like advancing front reported by Thomas and Windle is found since the iodine tracer used lagged the methanol absorbing into the PMMA samples. The absorption of the iodine tracer into the methanol swollen PMMA leads to the appearance of an advancing front [10,11]. That the iodine reached the center of the free film at the same time as methanol reached its saturation condition was a matter of chance found only at about 30°C, but not at higher or lower temperatures. The methanol had reached the center of the free film far earlier than the methanol as shown by the modeling in [11]. I am not aware of any other proposed explanations for a step-like, advancing front, but remain confident that any such could be resolved with the present procedure using solutions to the diffusion equation with no time dependent effects.

Conclusion

The data presented here cast considerable doubt on the conclusions given in [2]. It is this author's contention that the diffusion equation with a significant surface boundary condition and exponential diffusion coefficients can model the absorption and desorption of n-hexane in natural rubber and LDPE. Proof can be provided by measurement of concentration gradients, especially for NR samples, and/or measurement of diffusion coefficients at different concentrations.

References

- [1] Hansen CM. Understanding Absorption in Polymers: Key to Improving Barrier Properties. Presentation and Supplementary Text from talk at the 50th Nordic Polymer Days in Helsinki, May 29-31, 2013. www.hansen-solubility.com. Free Downloads.
- [2] Hedenqvist MS, Gedde UW. Parameters affecting the determination of transport kinetics data in highly swelling polymers above T_g . *Polymer* 1999;40:2381-2393.
- [3] Abbott S. Hansen CM. Yamamoto H. Hansen solubility parameters in practice: Complete with software, data and examples. Hoersholm Denmark: www.hansen-solubility.com; 1st ed. 2008, 2nd ed. 2009, 3rd ed. 2010, 4th ed. 2013. ISBN –978-0-9551220-2-6.
- [4] Forsberg K, Kieth LN. *Chemical Protective Clothing Performance Index, Second Edition*.
- [5] Marom, G. The role of water transport in composite materials, in *Polymer Permeability*, Comyn, J., Ed., Elsevier, London, 1985, chap. 9.
- [6] Hansen CM. Hansen solubility parameters: a user's handbook, 2nd ed. Chapter 16. Boca Raton FL: CRC Press; 2007.
- [7] Petropoulos JH Sanopoulou M Papadokostaki KG. Physically insightful modeling of non-Fickian kinetic energy regimes encountered in fundamental studies of isothermal sorption of swelling agents in polymeric media. *Eur Polym J* 2011;47:2053-2062.
- [8] Hansen CM. Response to the Criticism of Petropoulos and Coworkers, www.hansen-solubility.com. Feb. 22, 2013. Free download.
- [9] Hansen CM. In Defense of the Diffusion Equation, www.hansen-solubility.com. Feb. 22, 2013. Free download.
- [10] Windle, AH. "Case II Sorption" Chapter 3 in Comyn J. Ed., *Polymer Permeability*, Elsevier Applied Science, London, 1985. pp. 75-118.
- [11] Hansen CM. Reinterpreting Case II Absorption in PMMA, www.hansen-solubility.com. July 5, 2012.

See also:

Hansen CM. Doctoral Dissertation: The three dimensional solubility parameter and solvent diffusion coefficient, their importance in surface coating formulation. Copenhagen: Danish Technical Press; 1967. Free download from www.hansen-solubility.com.

Hansen CM. Diffusion in polymers. *Poly Eng Sci* 1980;20(4):252-258.

Hansen CM. The significance of the surface condition in solutions to the diffusion equation: explaining "anomalous" sigmoidal, Case II, and Super Case II absorption behavior. *Eur Polym J* 2010;46:651-662.

Hansen CM. Various free downloads: www.hansen-solubility.com. Especially: Surface Effects versus Bulk Phenomena as Explanations of “Anomalous” Absorption in Polymers.