

Reexamination of Super Case II – Data of Jacques, Hopfenberg, and Others

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Abstract

The experimental absorption data for n-hexane in polystyrene of Hopfenberg and coworkers [1-5] giving Super Case II behavior has been modeled by solving the diffusion equation with exponential concentration dependent diffusion coefficients and a significant surface condition. No consideration of stress relaxation or related phenomena was required for satisfactory modeling. The general features of the absorption curves were reproduced correctly with the elapsed times being very close and with an asymptotic approach to the final equilibrium value. There were no advancing fronts in these examples.

Additional examples are given to show that Super Case II absorption behavior is also possible with reasonably sharp, but not step-like, advancing fronts for the concentration gradients. This appears to be for situations where there is considerable concentration dependence of the diffusion coefficients and for absorption from the vapor phase to higher final concentrations.

Introduction

The studies of Hopfenberg and coworkers [1-5] on transport of alkanes in polystyrene form the basis of this analysis of Super Case II absorption into polymers (polystyrene). The example of the absorption of n-hexane into polystyrene has been considered a classical example of Super Case II absorption [2,5,6]. A frequently discussed figure is reproduced from [6] as Figure 1 in this document, but the same data are also included in Figure 2 as the lowest curve in the figure [2]. These data in Figures 1 and 2 are modeled in Figure 3 using the software in the HSPiP available from www.hansen-solubility.com [7].

These absorption experiments were done on 1½ mil (38 microns) films cast from trichloroethylene solutions with subsequent heating at 50°C to 55°C for 3½ days to remove residual solvent. It is shown that this procedure does remove the solvent. The prior history can be expected to affect the morphology of the films and the experimental absorption results. Long and more effective annealing will lead to a more coherent surface layer giving it more significance in absorption experiments. The equilibrium amount of n-hexane is enough to put the system very close to its glass transition temperature. The plasticizing effect of n-hexane on polystyrene is very strong [3]. Thus one might expect a strong dependence of the diffusion coefficient on concentration. It is also expected that once the linear n-hexane molecules enter the bulk of the film, they will be able to “worm” their way rather rapidly in comparison with non-linear molecules. The data for liquid absorption of n-hexane in polystyrene [4] cannot be processed since a stable equilibrium concentration is not specified.

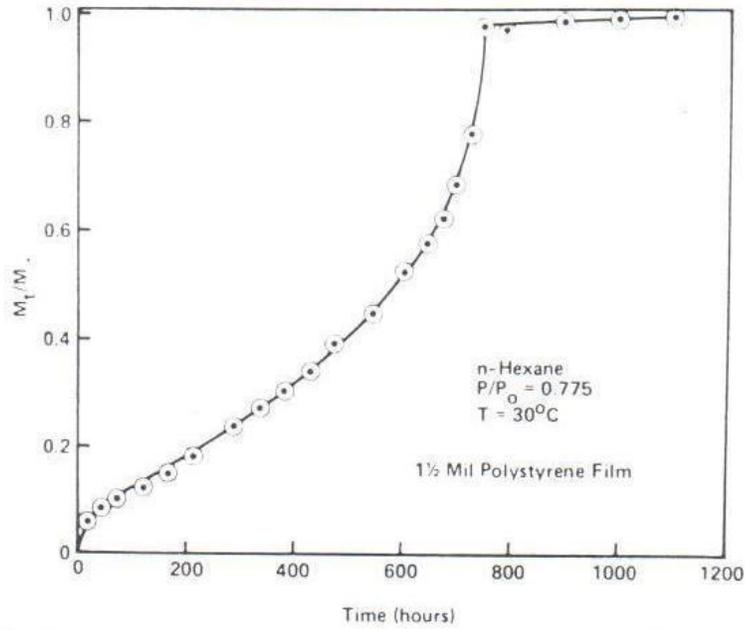


Fig. 22. Sorption plot for the *n*-hexane vapour (activity = 0.775)–polystyrene film (37 μm thick) system which shows Super Case II behaviour.⁴⁶

Figure 1. Absorption of *n*-hexane into polystyrene . From [6].

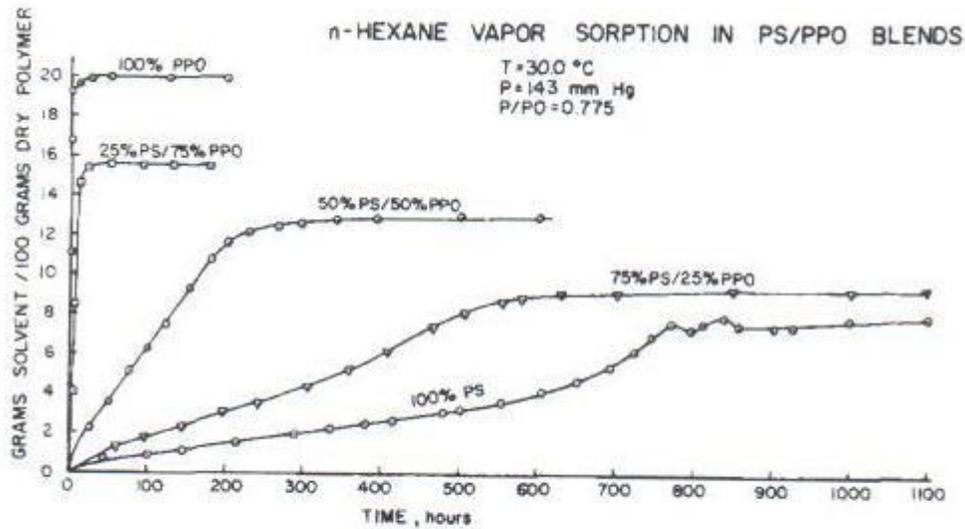


Fig. 3. Vapor sorption kinetics of *n*-hexane in PS/PPO polyblends.

Figure 2. Experimental data for the *n*-hexane in polystyrene system as reported in Figure 1 from [2]. The data for the uptake of *n*-hexane in polystyrene in this figure in the lowest curve.

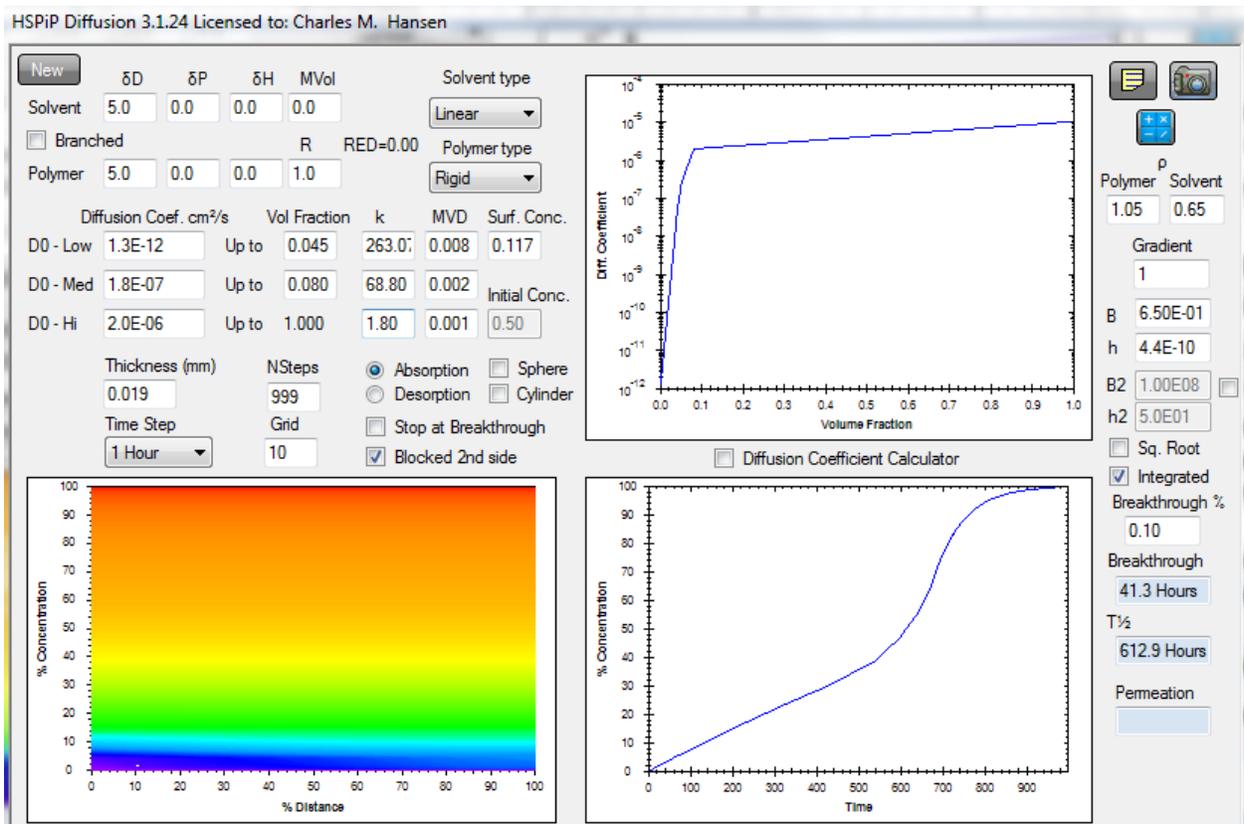


Figure 3. Modeling the Super Case II data in Figures 1 and 2 with the software from [7].

Figure 3 successfully models the uptake of n-hexane into a 1½ mil (38 microns) thick polystyrene film at 30°C at p/p_0 equal 0.775 using the data in [2,5,6]. The diffusion coefficient for n-hexane in polystyrene at this condition at the lowest concentration, D_0 , is assumed as $1.3(10)^{-12}$ cm²/s. The D_0 for n-pentane in polystyrene is given as about $3(10)^{-12}$ cm²/s at this temperature in [1], so this estimate is reasonable considering the slightly larger molecule. The entry mass transfer coefficient at the surface, h , ended after numerous iterations at $4.4(10)^{-10}$ cm/s.

The diffusion coefficients assumed are given in the upper right figure in Figure 3. These are described in more detail to the left in the figure. The uptake curve that is to be compared with Figure 1 or Figure 2 is at the lower right with the concentration gradients resulting from this analysis at the lower left. It can be seen from the flat concentration gradients that the surface condition dominates the absorption with diffusion in the film always being fast enough to rapidly remove the n-hexane into the bulk. The diffusion coefficients do influence the form of the absorption curve especially at higher concentrations, however.

The main features of the uptake curve in Figures 1 and 2 are present in Figure 3. The uptake is matched well at 200 hours, at 500 hours, and near the break at the top. The asymptotic approach

to equilibrium is also included, but not the very sharp break. This asymptotic approach to equilibrium has also been a result of a significant surface condition in past modeling. The initial short-time rise in the experimental data is missing. One could question whether this is real or experimental variation. See the discussion in the Supplementary Material as well.

Another example of the n-hexane absorption into polystyrene is given in Figure 4 reproduced from [1]. The data for n-hexane are given in the curve with the pronounced upward curvature typical of Super Case II. In this case the vapor pressure is such that the system is below its glass transition temperature. There is also a significant difference in the films, even though the same nominal 38 micron film thickness and temperature at 30°C are maintained. These films were cast from benzene and still contained 3% of the solvent distributed in the interior of the film. The surface concentration of benzene will be zero, and the concentration profiles of benzene in the interior will be reasonably flat. There is a relatively sharp drop in the concentration just within the surface. This is based on the modeling of the concentration gradients in film formation by solvent evaporation as has been done in [8,9]. The cast films were annealed at 110°C for 30 minutes and cooled by simply turning off the oven until it returned to room temperature.

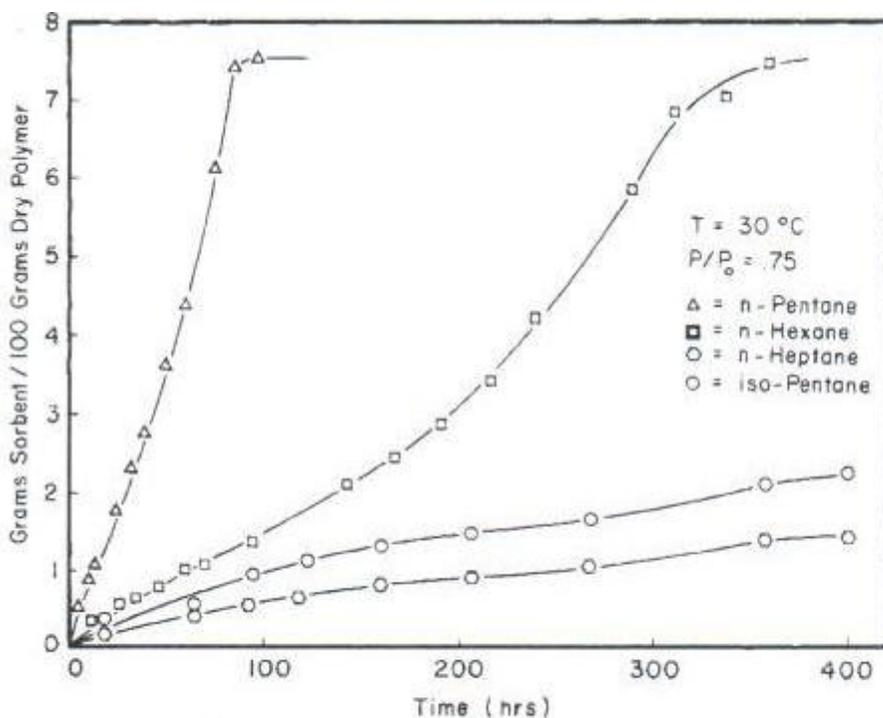


Fig. 10. Sorption kinetics of alkanes in cast, annealed polystyrene at constant temperature and penetrant activity.

Figure 4. Sorption of n-hexane into polystyrene at 30° at a condition where the temperature is below the glass transition temperature and the films still contain about 3% of the solvent benzene from which they were cast. Annealing was done for 30 minutes at 110°C.

The absorption of n-hexane reported in Figure 4 has been modeled in Figure 5. The surface condition dominates again demonstrated by the flat concentration profiles. The sharp increase in the diffusion coefficients with concentration is in part due to the retained solvent, but also to the strong plasticizing effect of the n-hexane as well as its ability to diffuse rapidly once in the film. D_0 is higher than in the previous example at $5(10)^{-12}$ cm²/s. This could be a result of the retained solvent or a different prior history or both. The surface mass transfer coefficient is also somewhat higher than in the previous example at $1.2(10)^{-9}$ cm/s. The effect of prior history is too difficult to analyze, but one might presume the annealing done in the first example is more complete. This would allow the polymer to orient to a condition of lower free volume with the polymer chain segments in the surface being more closely packed. This would provide lower diffusion coefficients and a lower surface mass transfer coefficient in the first example. It is concluded that this second experiment demonstrating Super Case II absorption behavior is also modeled satisfactorily.

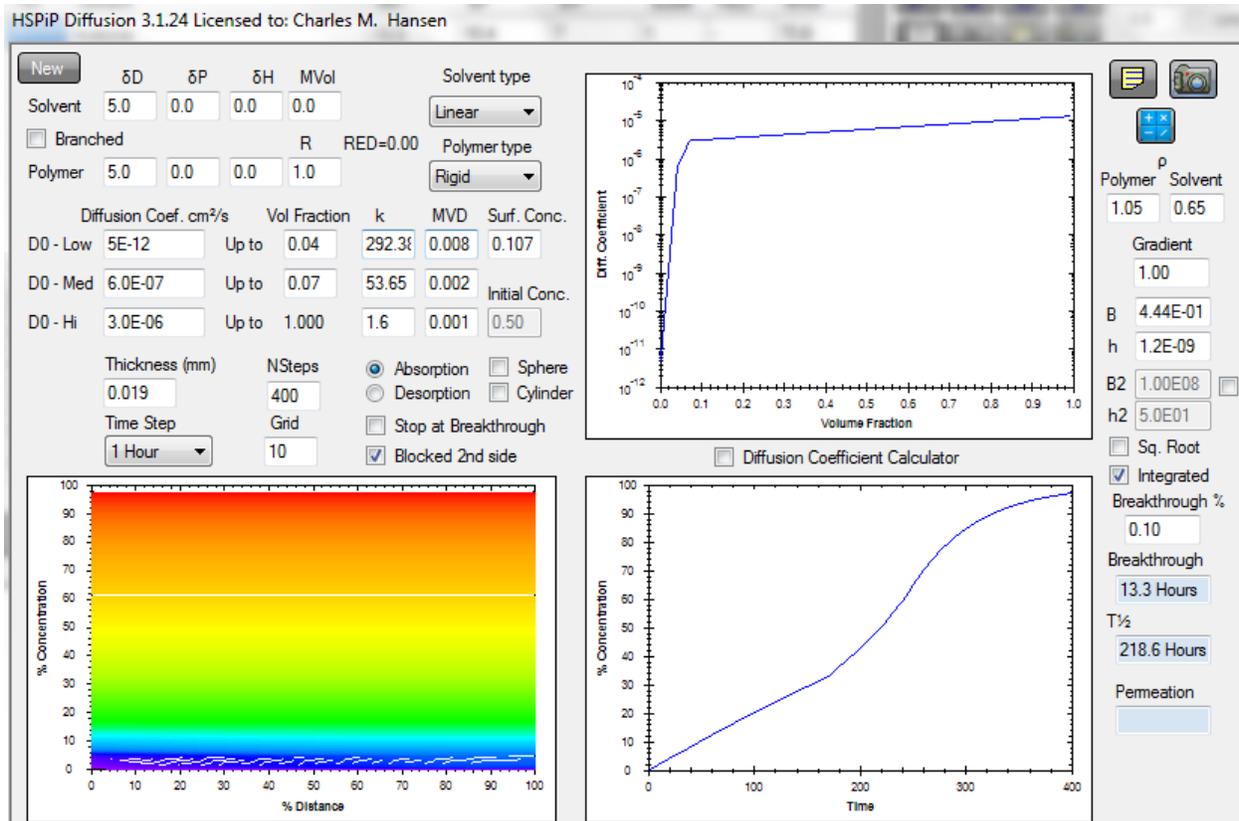


Figure 5. Model for the absorption of n-hexane into polystyrene using data from [1]. The experimental data that are matched by this figure are reproduced in Figure 4. The concentration gradients are again flat almost from the start showing the significance of the surface condition.

Additional examples of modeling Super Case II

Figures 6 and 7 give an example of modeling Super Case II diffusion reported by Windle [6].

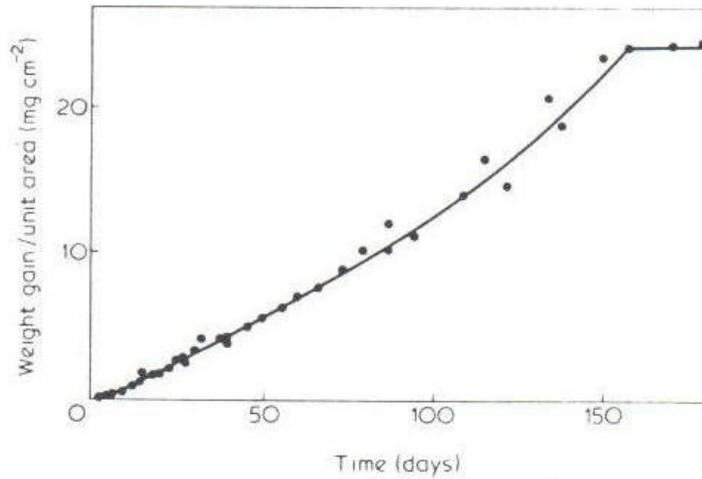


Fig. 23. Experimental sorption plot for PMMA-methanol at 0°C showing some acceleration in rate; the PMMA sheet was 1 mm thick.¹⁵

Figure 6. Super Case II behavior for the absorption of methanol in PMMA at 0°C [6].

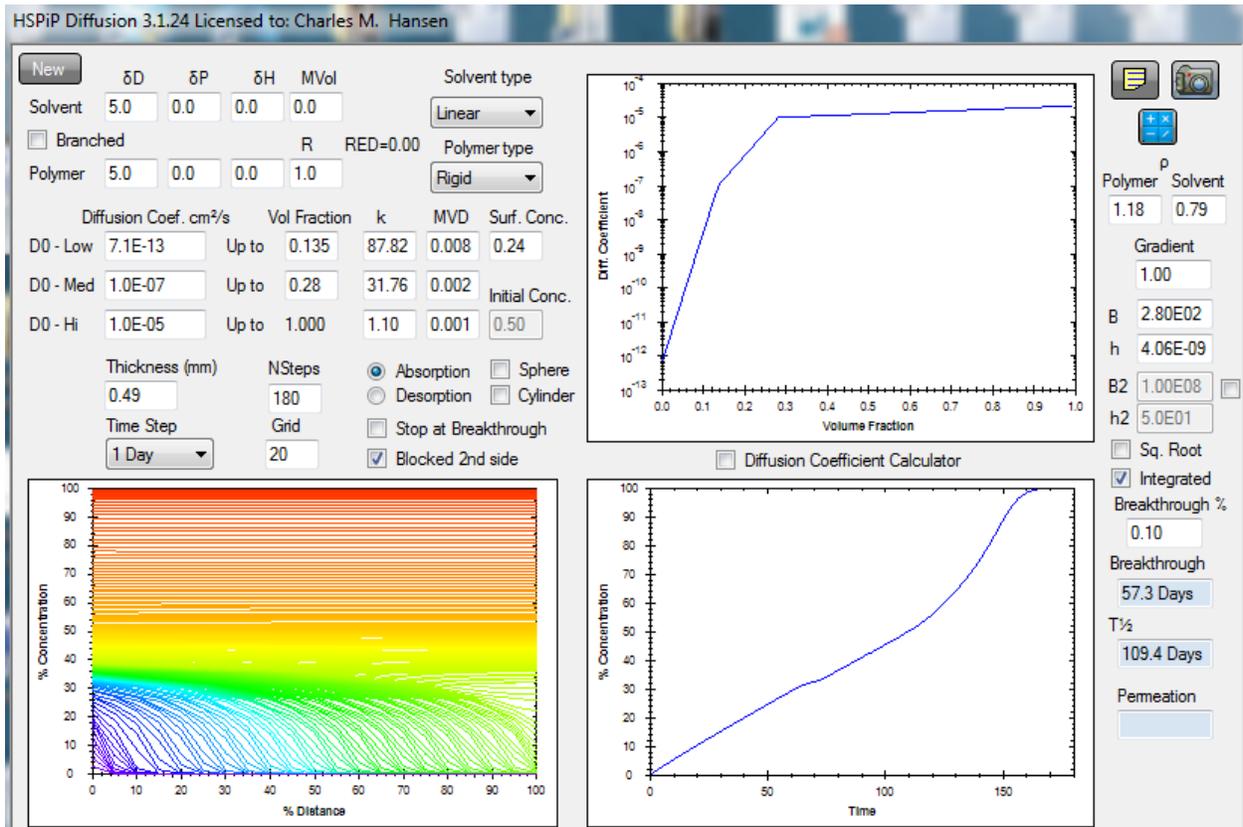


Figure 7. Simulated absorption of methanol into PMMA at 0°C [6] as reported in [10].

The absorption curve in Figure 7 can be fitted into the spread of data reported in Figure 6 for this experiment. The absorption curve bends upward and ends at about 160 days. Equilibrium absorption is 0.24 volume fraction. It is possible that other combinations of the variables would improve the fit, but the general trend is certainly confirmed. The uptake curve in Figure 7 is somewhat similar to what is shown in Figure 3, but the time scale is quite different. The surface condition is significant throughout, and in the last half of the absorption process the concentration gradients are flat. There is no advancing front as has been thought in the past for this kind of absorption curve. The use of iodine as a tracer for methanol in this system has been shown to be unsatisfactory since the iodine significantly lags the methanol giving an impression of a step-like advancing front [10].

The Super Case II examples shown in the following all involve an advancing front of some description, whereas the concentration gradients in the above examples are all flat after a short period where diffusion does have some control at the early stages. Instead of concentration gradients advancing into the film, the film is filled up with uniform concentration gradients throughout after a relatively short time.

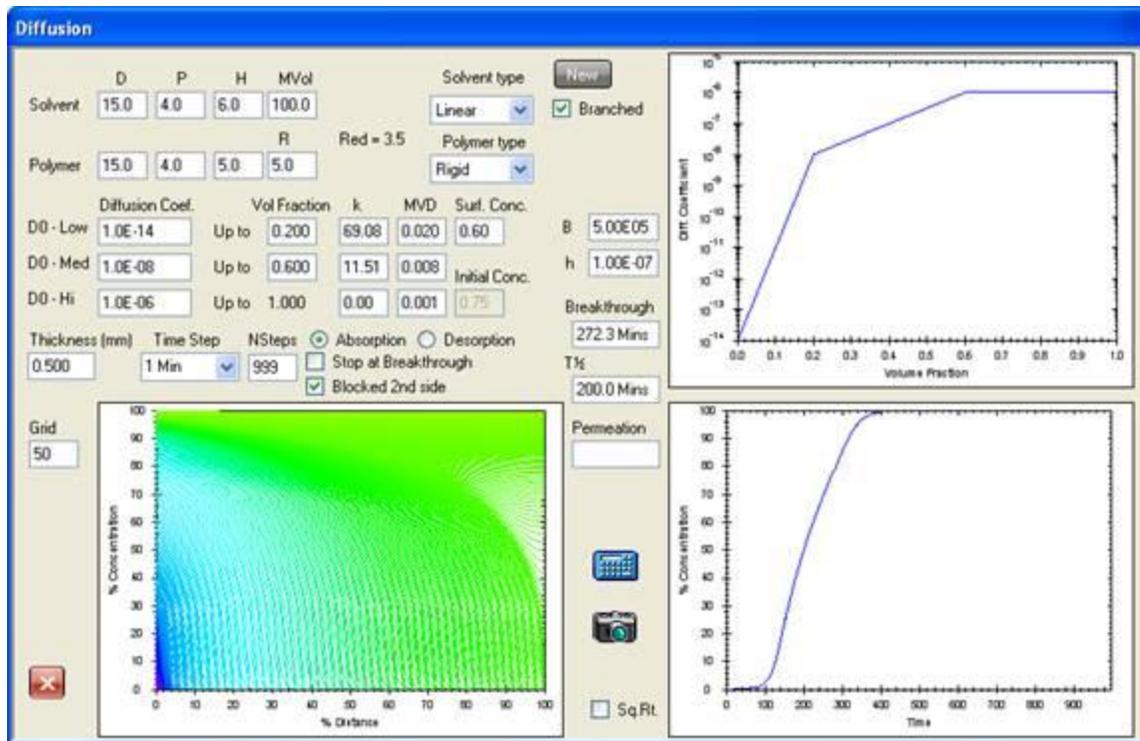


Figure 8. Simulation of Super Case II absorption using diffusion coefficients measured for the system chlorobenzene in poly(vinyl acetate) at room temperature [8, 11]. The surface mass transfer coefficient was assumed as $1(10)^{-7}$ cm/s and the equilibrium uptake at 0.6 volume fraction solvent. The concentration gradients approach the appearance of an advancing front.

Figure 8 uses measured coefficients for chlorobenzene in poly(vinyl acetate) at room temperature coupled with an assumed surface mass transfer coefficient equal to $1(10)^{-7}$ cm/s for a free film thickness of 1 mm. This leads to a marked increase in absorption rate at about 100 minutes, or well after the absorption process has started. There is a slow approach to the equilibrium value at the very end of the absorption process because the driving force for further absorption at the surface has become small. A significant surface condition in such cases can possibly be attributed in part to the surface entry resistance for larger molecules. Absorption at concentrations higher than 0.2 volume fraction in this system also led to S-shaped curves, i.e., a significant surface condition [12]. The value of h is $1(10)^{-7}$ cm/s. Some combination of the sources of significant surface condition resistance is also possible, if not probable, since the final uptake is rather high. The mathematical treatment is not able to distinguish the nature of a significant surface condition (surface entry, heat transfer, diffusion in external media), only that it is there.

An example of Super Case II diffusion is also found in Figure 9 that is reproduced from [12]. This is also theoretical and was developed to demonstrate what could reasonably be considered as advancing fronts can also be found with what is typically called Super Case II absorption. This is shown more clearly than in Figure 8. There was some question as to the ability of the diffusion equation alone to duplicate advancing fronts. Whether these advancing fronts at the lower left in Figure 9 satisfy given requirements is left to the reader. Here again the last stage of the absorption process is an asymptotic approach to the equilibrium value. There are no step-like concentration gradients, but such do not exist in the studies of Thomas and Windle either [10]. Likewise there is no need to consider stress relaxation or related phenomena as many would prefer. See also the Supplementary Material below.

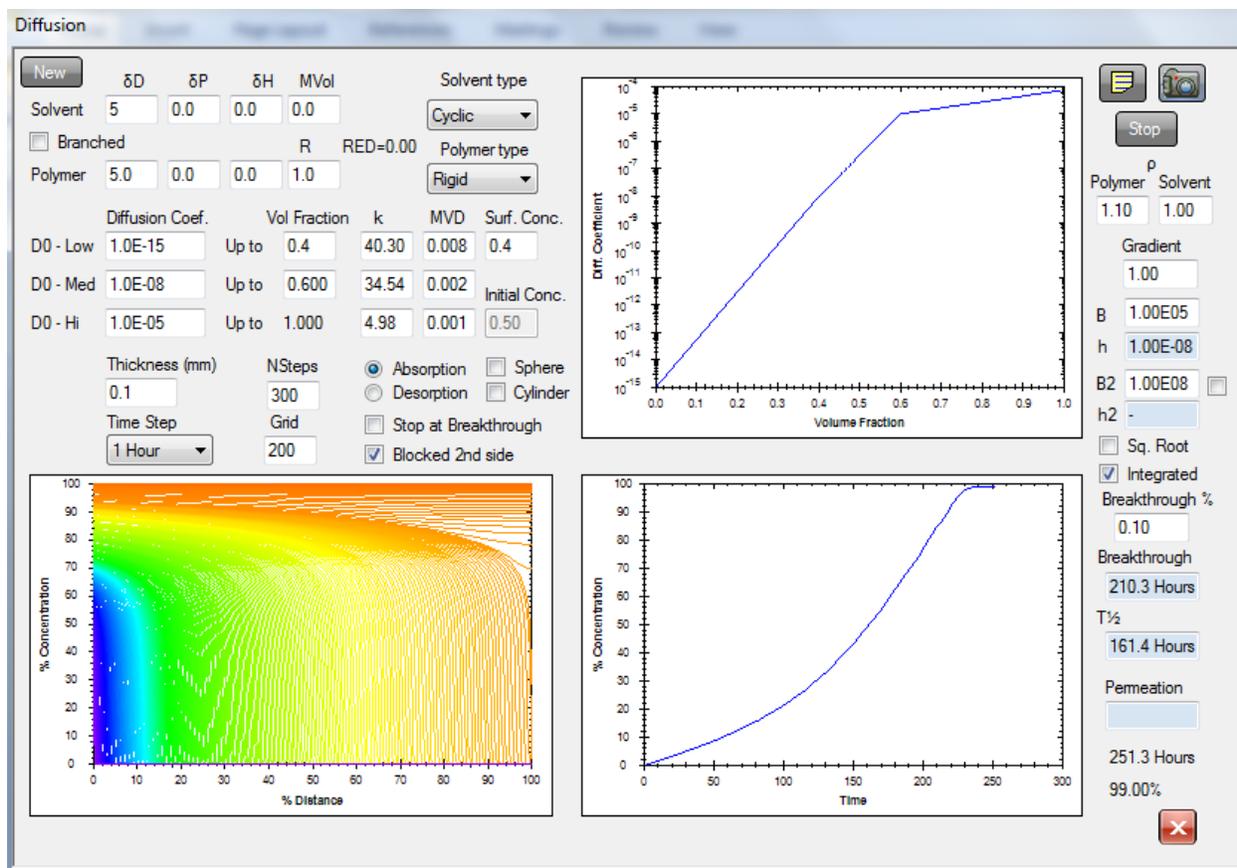


Figure 9. This figure models a theoretical experiment that shows Super Case II behavior with estimated, but realistic parameters. What could be considered advancing fronts in the concentration gradients can be seen at the lower left in Figure 9. The variable diffusion coefficients, surface mass transfer coefficient, and other parameters are reasonable.

The modeling in Figure 9 uses reasonable concentration dependent diffusion coefficients (upper right), and an estimated, realistic significant mass transfer coefficient $1(10)^{-8}$ cm/s. The diffusion coefficient at near zero concentration, D_0 , is assumed equal to $1(10)^{-15}$ cm²/s. This is somewhat lower than that normally encountered with more volatile liquids, but such values have been measured for the diffusion of cyclohexanone in poly(vinylacetate), for example [8,9,11], so it is realistic for larger or more bulky molecules. The “advancing front” concentration gradients are shown at the lower left. The absorption curve in this example closely resembles the shape of the absorption curve in Figures 1-3. The time to equilibrium is about 240 hours in this figure versus about 800 hours in Figures 1-3. This may be an example of an advancing front Super Case II system, but the last stage is controlled by the surface condition. It can be concluded that solutions to the diffusion equation appear to be able to model Super Case II with concentration gradients resembling advancing fronts, but they are not step-like. Such cases involve higher h values and higher equilibrium absorption values than the examples in Figures 1-5, where the uptakes are comparatively low. It appears that there can be many situations that are widely different in nature that can exhibit Super Case II absorption behavior.

A final comment is included from an excellent recent review by Vesely of the various theories of diffusion in polymers and techniques useful for understanding these phenomena [13].

“It can therefore be concluded that reproducible results can only be obtained by using the polymer from the same batch and of the same formulation, with identical thermal history. It means that the literature data can only be compared for a particular trend and not in their absolute values.”

Conclusion

The experimental absorption data for n-hexane in polystyrene of Hopfenberg and coworkers [1-5] giving Super Case II behavior has been modeled by solving the diffusion equation with exponential concentration dependent diffusion coefficients and a significant surface condition. No consideration of stress relaxation or related phenomena was required for satisfactory modeling. The general features of the absorption curves were reproduced correctly with the elapsed times being very close and with an asymptotic approach to the final equilibrium value. There were no advancing fronts in these examples. Quite to the contrary the concentration profiles were very flat with uniform concentrations at all distances from the surface, almost from the beginning of the experiments. There is a low surface entry mass transfer coefficient in these cases. This is thought to be partly if not totally due to the difficulty of adsorbing suitably at sites allowing entry into the bulk of the film. The behavior of the films is very much dependent on their prior history which makes predictions of behavior at other than tested conditions very difficult.

Additional examples are given to show that Super Case II absorption behavior is also possible with reasonably sharp, but not step-like, advancing fronts for the concentration gradients. This appears to be most likely for situations where there is considerable concentration dependence of the diffusion coefficients and for absorption from the vapor phase to higher final concentrations.

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July 14-20, 2012

Supplementary Material

The following should be incorporated into the main manuscript if it ever get published other than on www.hansen-solubility.com. The following has come about because of questions and comments from others as well as afterthoughts and discoveries by myself. The tone is perhaps a little different than in the original manuscript.

After having finished the manuscript there was a question as to the believability of the sharp increase in the diffusion coefficients with concentration. Why did it then take so long to saturate the films? And why was D_0 for polystyrene so low? At this point I can see no other alternatives than what is in the manuscript, but note that there is considerable variation in the properties of polystyrene when one examines some of the papers of Hopfenberg and coworkers.

In Ensore et al. [14] the equilibrium uptake at 30°C and n-hexane activity of 0.75 (below the glass transition temperature but close to this) is reported for spheres with small diameters. The spheres with 184 microns diameter absorbed 5 g n-hexane per 100 g polymer after a very long exposure, and there was some speculation as to a false equilibrium value. The polystyrene spheres with diameter 0.534 microns absorbed 9 g of n-hexane per 100 g of polymer at equilibrium. The difference was thought to be the result of subtle thermal and mechanical history effects. The uptake in the polystyrene films modeled in the manuscript for the same conditions was reported as 8.1 g per 100 g polymer by Jacques and Hopfenberg [3].

A search for literature values of the D_0 of n-hexane in polystyrene resulted in finding a value at 30°C for this equal to $1(10)^{-13}$ cm²/s, extrapolated as a value for a polymer of infinite molecular weight [15]. This diffusion coefficient would be about $2(10)^{-13}$ cm²/s for a polymer of moderate molecular weight. The method for finding these was the halftime of absorption to relatively low concentrations for monodisperse spheres. These values are somewhat lower than the $1.3(10)^{-12}$ cm²/s used in Figure 3. The feeling that the D_0 used is too low is therefore not justified by literature data as well as the results of this study. The experimental diffusion coefficients in such absorption studies would be expected to be a little low because of the combined effect of a significant surface condition as well as the diffusion resistance within the polymer. It is felt that the D_0 used in Figure 3 is essentially correct both for these reasons as well as the essentially correct modeling that has been done (see also the next paragraph).

As usual when writing such documents, one overlooks something that should have been seen at the start. The advantage of not having seen a piece of important information is that it can be used at a later time to confirm the validity of what was done. In the present case initial rates of uptake are reported in [2] for n-hexane into polystyrene at the conditions modeled here. The initial rate of absorption given in Figure 5 on page 84 in this source, and also given in the accompanying text, is $2.3(10)^{-4}$ mg/h cm². Using the approximate relation given in [16,17] for the surface mass transfer coefficient, $h = F_0/\Delta c_0$, gives h equal to $7.5(10)^{-10}$ cm/s. The value used in the modeling was $4.4(10)^{-10}$ cm/s. The value calculated here is probably higher because of a bias in the initial

slope most clearly seen in Figure 1. F_0 is the flux at the start of the experiment and Δc_0 is the concentration difference using the equilibrium value minus zero, preferably in g solvent/cm³ of dry polymer. This relation is probably reasonably accurate here since the surface condition is so dominant in this experiment. The agreement is surprisingly close, and further confirms the validity of the modeling. If one tries to use the calculated value for h , the absorption takes place too rapidly, and the difference cannot be countered by changes in the other parameters.

Finally, there remains a challenge to the theories where the absorption rate is exclusively controlled by phenomena in the bulk of the polymer. In the first example in the manuscript, a calculated average constant diffusion coefficient that would essentially saturate a 1½ mil free film after about 800 hours can be estimated with $D_0t/L^2 = 1$ as $1.25(10)^{-14}$ cm²/s. This relation is based on the solution to the diffusion equation for a constant diffusion coefficient for absorption to 95% of the equilibrium value [18]. This diffusion coefficient would have to prevail as an average in the experiment described in Figures 1-3, no matter which theory is applied to behavior in the bulk of the film. The effects of a stress relaxation mechanism, for example, would have to delay the rate of transport by a factor of 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 longer 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 interface. This 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, to put it mildly.

References in the supplementary material

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July 20, 2012