Understanding Absorption in Polymers – Abstract and Supplementary Text

Last Revision: May 23, 2013

Understanding Absorption in Polymers: Key to Improving Barrier Properties

Solutions for the diffusion equation with a significant surface boundary condition and diffusion coefficients exponentially dependent on local solvent concentration successfully modeled polymer film formation by solvent evaporation [1,2]. Solvent retention is caused by the very low diffusion coefficients at the low concentrations near the surface of a drying film. These early studies have been extended confirming the need for the surface boundary condition and exponential diffusion coefficients to explain what have been called “anomalies” of absorption in polymers [3-7]. Surface effects may delay absorption at short times only giving a sigmoidal (two-stage) process. In other cases (Case II/Super Case II) the surface condition can gradually dominate with initially slow diffusion becoming (exponentially) faster as absorption proceeds. Significant surface effects may be diffusion in stagnant air over the film or heat transfer to the film (evaporation) or from the film (condensation). Passing through the polymer surface itself can be limited or even stopped by large molecular size and/or irregular shape of solutes. Low equilibrium solubility means fewer suitable surface sites are available for the required adsorption, orientation, and absorption steps. A mismatch of the Hansen solubility parameters for the polymer and the solute improves barrier properties by reducing equilibrium uptake. This lowers concentration gradients, diffusion coefficients, and surface mass transfer coefficients. Examine these effects with an app: http://www.stevenabbott.co.uk/PracticalDiffusion/index.html

1. Hansen CM. Opløsningsmiddelretention i höjpolymere filmdannere og dens betydning for filmens mekaniske egenskaber, Svenska Kemistsamfundets Polymerdagar, Sept. 26-27, 1963. (Rånby B. Svensk Kemisk Tidskrift 1964;76:31-36.)

2. 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](http://www.hansen-solubility.com).

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

4. Hansen CM. Hansen solubility parameters: a user’s handbook, 2nd ed. Chapter 16. Boca Raton FL: CRC Press; 2007.

5. Abbott S. Hansen CM. Yamamoto H. Hansen solubility parameters in practice: Complete with software, data and examples. Hoersholm Denmark: [www.hansen-solubility.com](http://www.hansen-solubility.com); 1st ed. 2008, 2nd ed. 2009, 3rd ed. 2010, 4th ed. 2013. ISBN –978-0-9551220-2-6.

6. 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.

7. Hansen CM. Various free downloads: [www.hansen-solubility.com](http://www.hansen-solubility.com). Especially: Surface Effects versus Bulk Phenomena as Explanations of “Anomalous” Absorption in Polymers.

This document is to be read in conjunction with the power point presentation with the same title presented on May 30, 2012, in Helsinki at the 50th anniversary of what is now called Nordic Polymer Days. I decided to tell things exactly as I see them. Confucius said one can never convince a person by telling them they are wrong. Perhaps I am taking the wrong approach, but the major emphasis is intended to be on what is right, using experimental data interpreted otherwise (wrongly) in the past.

Slides 1-3: These slides tell why I am giving this talk in the first place. I am rounding out my activities in diffusion in polymers. A talk in Stokholm in 1963 at the first conference leading to what is now called the Nordic Polymer Days in 1963 was the starting point. This showed the diffusion equation can correctly model solvent desorption (film drying) when concentration dependent (exponential) diffusion coefficients are combined with a significant surface condition. The present talk shows the same approach correctly models solute absorption into polymers in spite of what the literature would lead one to believe. Typical examples are presented in the following to demonstrate this. I am amazed and disappointed that the general polymer community still has not accepted this simple result.

Slide 9: This equation says: What gets through the surface from the exterior phase is equal to what enters the bulk through the surface. This was erroneously interpreted in one case to read that the right hand side of the equation could at all times be substituted by the left hand side. It is emphasized that this is completely wrong. There are two resistances in series each of which is based on a different mechanism. The one may dominate initially but not at the last. In the following examples for Case II and Super Case II, for example, there is diffusion resistance at the start, but this becomes insignificant as concentrations increase and diffusion becomes very fast on a relative basis. These are then dominated by the surface entry effects. This kind of situation can also give sigmoidal (two-stage) absorption.

Slide 11: The basis for this slide is given in the following slides. It combines desorption, absorption, isotope studies, and the self-diffusion coefficient into diffusion coefficients covering all concentrations for the system.

Slide 13: This slide is discussed in detail in previous publications, the earliest being an article in the Journal of the Oil and Chemists’ Association. Hansen, C.M., A mathematical description of ﬁlm drying by solvent evaporation, J. Oil Colour Chem. Assn., 51(1), 27–43, 1968. The basis is also found in the Doctoral dissertation (free download from website). There is also discussion in Chapter 16 of the second edition of the CRC Handbook. There was more rapid loss in the climatized room because of water absorption. When the desorption was done under vacuum in the absence of water, which was how the diffusion coefficients were measured, the agreement between calculated and experimental drying was excellent.

Slide 14: The data here were taken from the Doctoral thesis based on long time retention in poly(ethyl methacrylate), poly(vinyl acetate), and the vinyl acetate/vinyl chloride copolymer VYHH (Union Carbide).

Slide 16: The sigmoidal shape is the result of the surface resistance becoming significant for this absorption experiment. Corrections were made for both surface resistance and concentration dependence to get a final result in agreement with the other data. This point is given in purple in the previous figure.

Slide 17: The data used in this slide were found in: Hasimi A, Stavropoulou KG, Papadokostaki M, Sanopoulou M. Transport of water in polyvinyl alcohol ﬁlms: effect of thermal treatment and chemical crosslinking. Eur Polym J 2008;44: 4098–107. The interpretation in this reference is based on a stress relaxation mechanism. This figure is taken from the second reference in the previous slide: 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. This then led to a demonstrative protest from the Petropoulos group as referenced in the next slide. I do not see how one can absorb water from the vapor phase from bone dry polymer to a liquid with relatively low viscosity and call it controlled by stress relaxation. The surface mass transfer control mechanism reproduced the experimental result with no problem, although diffusion coefficients were assumed based on related systems to do this.

Slide 19: Note that the absorption of THF was very rapid to a very high final concentration and there was essentially no sigmoidal shape for the curve. These data were analyzed for the surface mass transfer coefficient using the initial flux and maximum concentration difference over the surface. Data for h are given in the following.

Slide 22: These data are very significant showing that h depends on the probability of finding a site for absorption. These sites are presumed proportional to the equilibrium uptake. Low uptake then leads to low h. The h for THF was estimated since the experiment was dominated by diffusion, thus leading to an apparent h that is clearly too low, because the method for finding the apparent h assumes there is no diffusion resistance. As shown in Slide 8 one divides the initial flux by the maximum (initial) concentration difference over the surface to find h. When diffusion is the cause of essentially all of the resistance at the surface, the h estimated in this way will be too low since the total effect is assumed to be surface resistance controlled.

Slides 24-30: The Thomas and Windle data re-examined here show that the step-like advancing front concentration gradients they report for absorption of methanol into PMMA does not exist. The mechanisms proposed by those who have attempted to reproduce this by modeling bulk properties only are not correct. The concentration gradients are in fact horizontal. This is discussed in more detail in a free download from my website called “Reinterpreting Case II absorption in PMMA”. I show the diffusion coefficients for the tracer iodine in methanol swollen PMMA are much lower than those of methanol. This is also expected from literature data shown in slide 30. This slide shows the effect of molecular size on diffusion coefficients for PVC at very low concentrations. The diffusion coefficients for methanol that were required to match the uptake curve also agree with what is expected from literature data. It could be mentioned that at higher temperatures than those giving the straight line uptake with linear time, the uptake shows more tendency toward sigmoidal absorption. At lower temperatures than the 30°C used to demonstrate Case II one finds an increased tendency to an increasing rate on a linear time plot of absorption. Such a case is included in the document that can be downloaded free from my website called “Reexamination of Super Case II”.

Slides 31-32: There is still another download on my website that explores the frequently cited work of Hopfenberg and coworkers for Super Case II called “Reexamination of Super Case II”. The initial rate of uptake reported in the original work is very closely duplicated here by the required parameters for matching the uptake curve at various elapsed times. The initial uptake is smoothed in the modeling. The initial higher rate at the very start may be real (perhaps caused by some rearrangement of surface polymer chain segments) or experimental variation. There was some retained solvent in these samples that would account for a more rapid increase in the diffusion coefficients with concentration that otherwise expected. The was also considerable variation in other properties of these polystyrene samples as reported in other articles by the Hopfenberg group. At any rate the concentration gradients show the surface condition is still more important than in Case II absorption, and the diffusion equation solved with verifiable and reasonable parameters can explain the phenomena.

Slides 33-36: These slides relate to the article in the European Polymer Journal that is cited. I was able to completely match the data for dichloromethane absorption into the stretched and confined cellulose acetate films in the direction perpendicular to stretching. This was simply a matter of concentration dependent diffusion coefficients with no significant surface resistance. I matched the precursor in the experiment for absorption parallel to the direction of stretching, but could then not completely account for the very high diffusion rates from the exposed surface to the top of the advancing front. The Greek group emphasized matching the flat concentration profile at highest concentrations while presenting a rather poor match for the precursor at the same time. I have estimated the diffusion coefficient required to give the flat curve at the high concentrations from the data presented to be about 5.5(10)-5 cm2/s. This is about 3 times higher than that expected for the self-diffusion of liquid dichloromethane. The experiment is not under control as assumed. There is a much more complete discussion in a download on my website called “Response to the Criticism of Petropoulos and Coworkers”. This is largely based on cellulose acetate having very rigid molecules. When they are stretched they orient parallel to each other with many contacts to neighboring molecules. This means no extensive polymer chain segment motion is possible until a given concentration is achieved (about 5% in this case). When this limit is reached, diffusion coefficients increase very rapidly. Matching the flat profile at the high concentrations implies very high diffusion coefficients at this condition, which cannot be treated in the software used. I suspect there may be channeling or similar phenomena at the highest concentrations allowing more rapid solvent entry/penetration than strictly diffusion would allow.

Additional slides after the completion of the planned talk:

Slides are included to show the treatment of permeation. Diffusion coefficients for permeation of various chemicals through various types of chemical protective gloves are reported in the HSPiP available from my website.

There is a slide showing how to determine the significance of edge effects. See also the second edition of the handbook in Chapter 16.

There are slides for other conditions that would give the appearance of Case II and Super Case II. There are numerous combinations of parameters that can do this, but the general effects are brought about by the increase in the diffusion coefficients with concentration as time goes on, coupled with a surface resistance that is perhaps significant from the start, but at any rate becomes significant on a relative basis as time goes on.

There are slides summarizing the HSP concept just in case.

|  |  |
| --- | --- |
|  |  |