METHANOL PMMA ABSORPTION WITH HORIZONTAL CONCENTRATION GRADIENTS

ABSTRACT

The absorption of methanol into PMMA follows a straight-line curve when plotted against linear time [1,2]. Concentration dependent diffusion coefficients and a significant surface entry mass transfer coefficient were used in the diffusion equation to fit this curve. The results confirm a slowly rising surface concentration with concentration gradients becoming horizontal after about half of the equilibrium absorption uptake.

BACKGROUND

The diffusion equation has a general derivation which states that the flux in minus the flux out equals the accumulation. It is fully capable of describing diffusion in polymers. Concentration dependent diffusion coefficients are allowed. Diffusion coefficients exponentially dependent on local concentration are found for the diffusion of solvents such as methanol in polymers such as polymethyl methacrylate (PMMA). Two boundary conditions are required for solving the diffusion equation. One of these is usually taken at the center of the film (or disk) for a two-sided absorption since there is no mass transfer at this point. The second boundary condition is that for the exposed surface. The usual assumption is that the solvent concentration in the surface, cs, immediately rises from zero to the equilibrium value c∞. While this may be true in many cases, it certainly is not true for the absorption of methanol into polymethyl methacrylate (PMMA). Thomas and Windle [1,2] found that methanol absorption into PMMA at 30˚C follows a straight line when plotted against linear time. They used a tracer that indicated concentration gradients were vertical, step-like as they advanced into the film. The present analysis based on solutions to the diffusion equation shows that the surface condition ultimately controls absorption, such that horizontal concentration gradients are found for the last half of the absorption process. The step-like advancing front is an artifact of a tracer that diffuses too slowly compared to the methanol. At longer exposure times the methanol entering the PMMA diffuses rapidly throughout the bulk giving horizontal concentration gradients. See Figure 1.

SOLUTIONS TO THE DIFFUSION EQUATION WITH A SIGNIFICANT SURFACE CONDITION

While it may seem complicated to analyze absorption curves using concentration dependent diffusion coefficients, D(c), and surface entry coefficients, h, this is not the case. Relevant solutions to the diffusion equation for this kind of situation are readily generated using the validated software in the software package and eBook called HSPiP (Hansen Solubility Parameters in Practice). The HSPiP is available from [www.hansen-solubity.com](http://www.hansen-solubity.com). The straight-line absorption curve with linear time found by Thomas and Windle for methanol absorption into PMMA films at 30˚C provides enough data to do the job. One makes a trial solution with assumed values and then systematically improves the assumptions with further iteration until the modeled absorption curve closely matches the straight line with time found in the experiment. The modeling took about one-half hour. The surface boundary condition is very significant. Figure 1 is a screen shot of the results of this analysis. The settings for the analysis are in the upper left section. The diffusion coefficients are shown at the upper right. The concentration gradients are at the lower left, and the match for the linear absorption curve is at the lower right. The modeling required h equal to about 11(10)-7 cm/s. The diffusion coefficients in cm2/s changed exponentially from 5(10)-11 at near zero concentration to 1(10)-7 at 0.11 volume fraction in the “solid” region. They follow a new exponential curve in the “elastomeric” region rising to a concentration of 0.2 volume fraction. Then follows an estimated 1(10)-5 in the “liquid” region. Note that the diffusion coefficients at higher concentration than the saturated condition at 0.265 volume fraction are not relevant but are necessary to complete the required data input. The surface condition completely controls the absorption process after the surface concentration rises to about 0.12 volume fraction and higher. Smaller errors in the modelled diffusion coefficients at concentrations above this are therefore not significant. Diffusion here is rapid enough to lead to horizontal concentration gradients.

EXPERIMENTAL DATA FROM THE LITERATURE

The mass flux through the polymer surface, Fs, is equal to the surface entry coefficient, h, times the concentration difference at the surface.

Equation 1 Fs = h(c∞ - cs)

h can be estimated from experimental absorption measurements. cs is zero at time zero, so one can estimate h by dividing the measured mass flux extrapolated to zero time by c∞. The data of Thomas and Windle are particularly easy to use in this respect since the straight-line absorption (flux) with time prevails over almost the entire absorption curve. The h derived from this (constant) experimental flux is 5.6(10)-7 cm/s. In this kind of experiment with numerous possibilities for variations this is very close to the value modeled above, that being 11(10)-7 cm/s. The difference is insignificant in the overall picture.

Concentration gradients for the absorption of methanol through the edges of PMMA disks were reported recently [3]. The modelled diffusion coefficients and h from the experiments on films of Windle and Thomas were used to see how closely they would predict the behavior for disks in this study. The calculated absorption and concentration gradients closely followed the reported results. The “breakthrough” times (when the solvent reached the center of the test specimen) were calculated as about 21 hours versus the experimental at about 18+ hours. The concentration gradients were very similar. Unfortunately, this difficult-to-perform experiment was not (or could not be with strict control) carried to full saturation. It is a logical conclusion that horizontal concentration gradients at concentrations higher than about half of the potential equilibrium uptake would be found if they were (or could be) measured.

This and other examples demonstrating the importance of surface entry resistance have been examined in more detail in documents that can be downloaded from the hansen-solubility website. A power point presentation called “Diffusion in Polymers 2020” summarizing the author´s views with examples is also available as a download [4].

h for various solvents are reported for their absorption into the COC polymer Topas® 6013 for liquid contact [5]. These h values are given in Table 1 and Figure 2. They were found from the s-shaped absorption curves in the manner described above using the flux at time zero+. There is a clear exponential dependence of h on the amount of solvent that can be dissolved in the polymer at equilibrium absorption. The higher the potential solvent uptake, the higher the surface entry coefficient. While it may be a matter of chance, the h predicted by Figure 2 for an equilibrium uptake of 0.265 volume fraction (the equilibrium value for methanol in PMMA) is 7(10)-11 cm/s, which is essentially that found in the above in the analysis.

DISCUSSION

The diffusion coefficients and h values determined in this analysis of the absorption of methanol in PMMA agree with what is expected from similar data in other systems. The absorption curve is matched with a constant h. This supports the view that the polymer surface exposed to the methanol always has the same orientation. As given molecules of methanol, or other solvent, find a suitable site for absorption, they must align and get into the surface itself. At this point forward movement is dictated by the local concentration just within the surface and the local diffusion coefficient. The given molecule could also just back out. When molecules do get through, the polymer surface molecules return to their original orientation and the same h values prevail for essentially all concentrations within the bulk of the polymer. At some high concentration this may break down, but experimental data are lacking for any conclusion on this point. The surface control leads to a tailing of the absorption curve in the final stages. There are indications that higher equilibrium solubility provides more potential entry sites at the polymer surface, and less surface resistance to absorption, but this needs further study.

SUMMARY

The diffusion equation successfully models the absorption of methanol into PMMA at 30˚C using the data of Thomas and Windle [1,2]. A significant surface entry mass transfer coefficient is required as are diffusion coefficients exponentially dependent on the concentration of the diffusing species. This leads to horizontal concentration gradients after about one-half of the equilibrium absorption.

The only experimental information needed for the analysis was the data for the straight-line absorption with time reported by Thomas and Windle [1,2]. If one lacks diffusion coefficients and/or surface entry coefficients, a simple way forward is to measure weight gain with time. Any deviation from a straight line versus square root of time plot is a sign there is a surface condition that is significant. The absorption curve can then be matched by assuming D(c) and h values which can be changed systematically until a good match is found in the modeling. The ability to find such rapidly obtained solutions for the diffusion equation is provided in the HSPiP.

A full literature review of diffusion in polymers is beyond the scope of this communication. It is anticipated that additional experimental confirmation of the concept presented here will be forthcoming.

POTENTIAL CONFLICT OF INTEREST

None

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

LITERATURE

1. A. H. Windle, Case II sorption. In Polymer Permeability; Comyn J. Ed.; Elsevier Applied Science: London, 1985, pp. 75-118.

2. N. L. Thomas, A. H. Windle, Transport of methanol in poly(methyl methacrylate). *Polymer* **1978**, 19(March), 255-265.

3. J. Nixdorf, G. Di Florio, L. Bröckers, C. Borbeck, H. E. Hermes, S. U. Egelhaaf, and P.Gilch, Uptake of Methanol by Poly(methyl methacrylate): An Old Problem Addressed by a Novel Raman Technique, *Macromolecules* 2019, 52, 13, 4997-5005.

4. Diffusion in Polymers 2020 power point presentation. [Diffusion in Polymers 2020.pptx](https://www.hansen-solubility.com/contents/DIFFUSION_IN_POLYMERS_2020.pptx)

5. T. B. Nielsen, C. M. Hansen, Significance of surface resistance in absorption by polymers. *Ind. Eng. Chem. Res.* 2005, 44(11), 3959-3965.

Additional literature on the need for the surface condition with the diffusion equation for interpreting diffusion in polymers:

Hansen solubility parameters: a user’s handbook, 2nd Ed.; Hansen, C. M. Ed.; CRC Press: Boca Raton FL, 2007. Chapter 16.

C. M. Hansen, Diffusion in polymers. *Poly. Eng. Sci.* 1980, 20(4), 252-258.

C. M. Hansen. 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.

Table 1. Apparent surface entry mass transfer coefficients and equilibrium uptake for solvents in a COC polymer Topas 6013® (Ticona) as reported in (5). A plot of these data is given in Figure 2. The value for tetrahydrofuran shown in Figure 2 is higher than that given in the table based on an estimate.

Solvent Apparent h, cms-1 Equilibrium uptake, volume fraction

Tetrahydrofuran 1.89(10)-4 0.676

Hexane 7.78(10)-6 0.351

Diethyl ether 1.21(10)-6 0.268

Propylamine 1.49(10)-7 0.181

Ethylene dichloride 1.18(10)-7 0.176

Ethyl acetate 1.46(10)-8 0.076

n-Butyl acetate 8.30(10)-10 0.202

FIGURES 1-2 FOLLOW



Figure 1. Screen shot from the HSPiP software for the modeled absorption of methanol into PMMA at 30˚C. Experimental data from (1,2). See text for more detailed explanations.

Figure 2. The surface mass transfer coefficient for solvents of smaller molecular volume in COC (Topas® 6013) depends on the equilibrium absorption. See Table 1.