Reinterpreting Case II Absorption in Polymers - An Examination of the Thomas and Windle Data

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Abstract

The use of iodine as a tracer for methanol diffusing in polymers is unsuitable and has led to erroneous conclusions. The step-like gradients advancing at a linear rate with time that have been thought to be an inherent part of Case II type absorption in polymers are not found in this analysis of the data for the characteristic examples of Thomas and Windle. The diffusion equation solved with an exponential concentration dependent diffusion coefficient and a significant surface condition is shown to reproduce the experimental data for weight gain at the same time demonstrating the lack of step-like concentration gradients. The surface condition appears to be particularly important in the methanol/PMMA systems studied by Thomas and Windle. Methanol “fronts” meet at the center of a free film much more quickly than the iodine tracer “fronts".

Nature will try to reduce the surface free energy of the polymer by forcing hydrocarbon entities to the air surface. The methanol molecule preferentially orients toward a hydrocarbon rich PMMA surface with the methyl group being the adsorbing end. Since the alcohol group is expected to be in the preferred direction of diffusion, this reversed preferential adsorption presents an added retarding effect to passing through the surface. The methanol molecule must orient into a suitable receptor space (not a polymer chain) and subsequently diffuse into the bulk. This kind of surface effect is self-restoring since the PMMA chains can move and/or rotate, and the methyl groups will continue a preferential orientation toward the polymer surface. This appears to be a reason for the satisfactory modeling done here with a constant surface mass transfer coefficient.

Key Words: Case II absorption, concentration gradients, diffusion equation, anomalous diffusion

Introduction

What is conventionally called Fickian absorption is characterized by an initial linear uptake of the diffusing material when a plot of the square root of time is used. The equilibrium concentration is assumed to be reached immediately at the start of the experiment. The concentration gradients all start at the surface at this concentration and proceed into the bulk according to the given situation. In given situations plots using the square root of time do not represent the experimental data. Such cases have been called “anomalous” and include sigmoidal, (time-lag or S-shaped), Case II (with linear absorption rate with linear time), or Super Case II (where the absorption rate increases with linear time). This report mainly concentrates on an interpretation of Case II absorption that is not in agreement with what is generally accepted. Step concentration gradients advancing linearly with time are a traditional identifier of Case II absorption. This report gives an alternate explanation for the apparent step-like advancing fronts in the absorption experiments of N. L. Thomas and A. H. Windle [1-7]. There are many other examples of Case II absorption in the literature, but the very thorough work of these researchers and their reporting of the required data are compulsive to anyone looking for an alternate explanation. Again, the results of Thomas and Windle are frequently cited as a typical example of what is called (anomalous) Case II absorption in polymers, and indeed the title of the chapter in [1] is "Case II Sorption" in agreement with this.

Thomas and Windle thoroughly explored the absorption of methanol in PMMA at many conditions [1-7]. The experimental data chosen by Windle in [1] for an expanded discussion of Case II absorption are for the absorption of methanol into PMMA at 30°C. Figures 1 and 2 are taken from [1] but are reproduced from [3]. Figure 1 shows the concentration gradients found by using iodine as a tracer for the methanol, and Figure 2 shows the methanol uptake curve for these data. It can be seen that the concentration gradients appear to be advancing fronts with a step-like profile. Figure 2 shows a linear uptake on a plot using linear time. Again, these results are typical of what is called Case II absorption and were chosen by Windle as "an excellent example of Case II behavior".

A main point of the discussion by Windle [1] is that for the absorption of methanol into PMMA at 30°C, there is an extremely sharp advancing front followed by a very flat concentration profile at the higher concentrations in the experiment. The concentration gradients are reminiscent of a cliff with a direct drop off. Such step-like concentration profile data cannot be reproduced by the methodology outlined for Case II type absorption in [8,9]. This has led to reviewer comments which are addressed in this document. The approach presented in [8,9] uses solutions to the diffusion equation which may include exponential concentration dependent diffusion coefficients as well as a potentially significant boundary condition. This approach does reproduce all the aspects of "anomalous" diffusion in polymers (sigmoidal, Case II, and Super Case II) except for the precipitous advancing front discussed above [8]. In the following it will be shown that a significant surface effect is required for the linear uptake with time characteristic of Case II absorption shown in Figure 2 for the uptake of methanol in PMMA at 30°C. Concentration dependent (exponential) diffusion coefficients are also required.

The features in Figures 1 and 2 are explained in great detail in [1] in a theory which is not supported by this analysis. The reader is referred to [1] or to other articles by Thomas and Windle for this theory. Quoting from [1] "Case II sorption occurs over a range of conditions for which there is both diffusional and deformation (often called relaxation) control." It has been common to use two separate equations or to add terms onto the diffusion equation to simulate this behavior. It should also be noted that there have been many theories proposed in this respect, with an excellent review of the earlier ones being given in [5]. A more recent extended review of current theories has been given by Vesely [10]. It is beyond the scope of this report to examine each of these. Indeed Vesely has commented as to the extent of their successes. It is the author's contention that stress relaxation need not be considered to explain the various forms of "anomalous" diffusion.

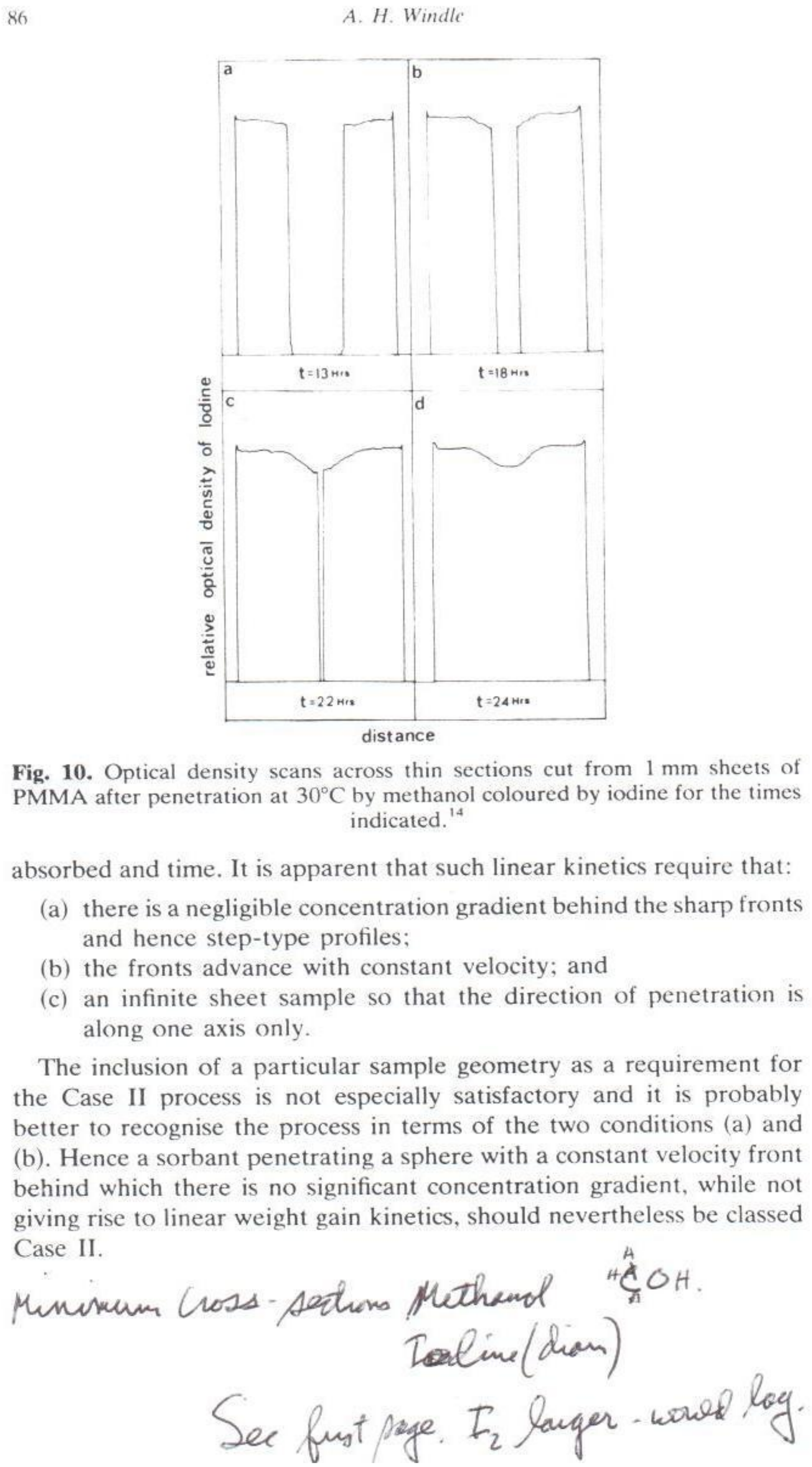

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Fig. 10. Optical density scans across thin sections cut from 1 mm sheets of PMMA after penetration at 30°C by methanol coloured by iodine for the times indicated.[14]

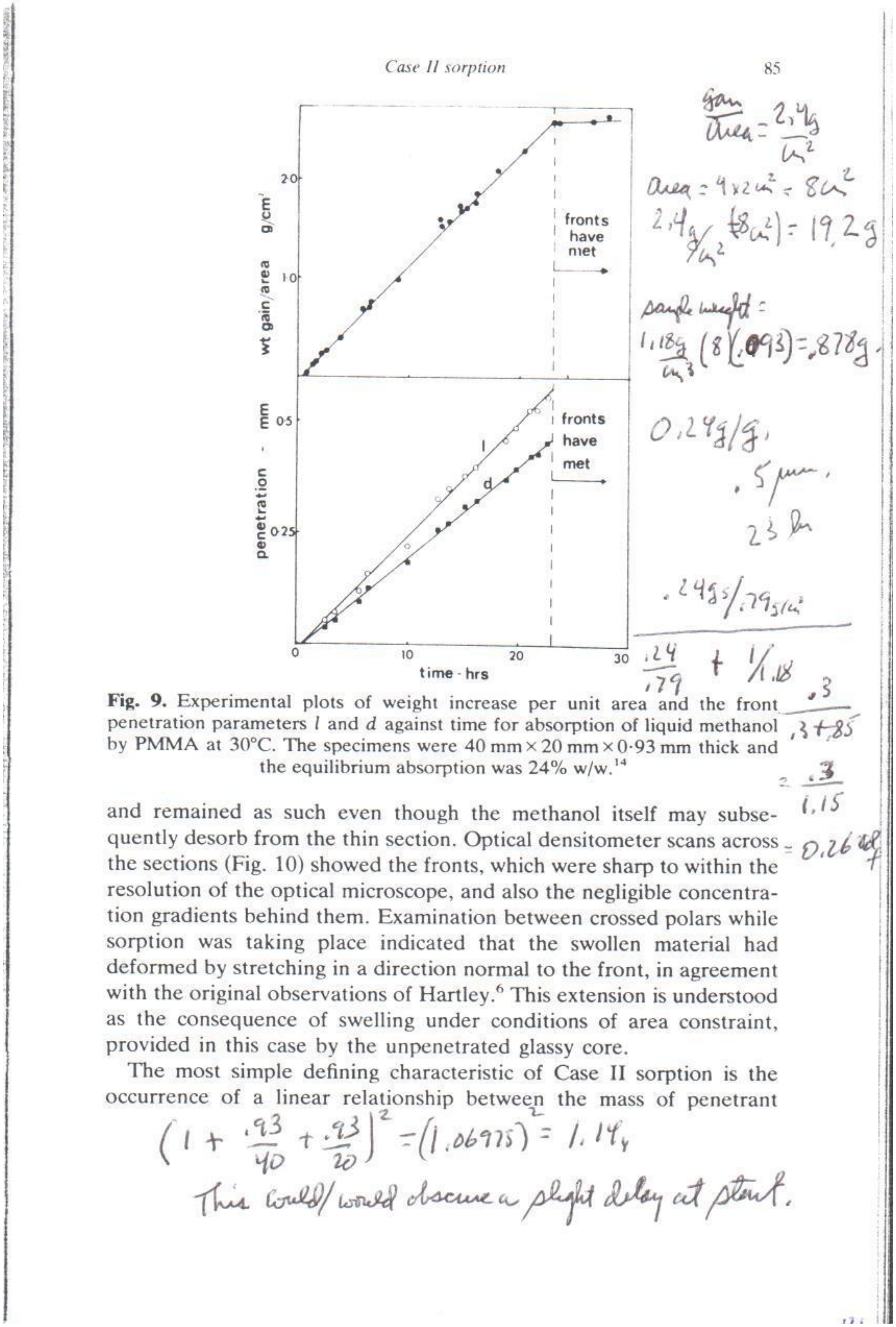
absorbed and time. It is apparent that such linear kinetics require that:

(a) there is a negligible concentration gradient behind the sharp fronts and hence step-type profiles;
(b) the fronts advance with constant velocity; and
(c) an infinite sheet sample so that the direction of penetration is along one axis only.

The inclusion of a particular sample geometry as a requirement for the Case II process is not especially satisfactory and it is probably better to recognise the process in terms of the two conditions (a) and (b). Hence a sorbant penetrating a sphere with a constant velocity front behind which there is no significant concentration gradient, while not giving rise to linear weight gain kinetics, should nevertheless be classed Case II.

Minimum Cross-sections Methanol $\overset{\mathrm{H}}{\underset{\mathrm{H}}{{}^{\mathrm{H}}\mathrm{C}}}\mathrm{OH}$.
Iodine (diam)
See first page. I_2 larger - would log.

Figure 1 (above). A copy of page 86 of reference [1] including some thoughts expanded upon in the following.



$\frac{\text{gain}}{\text{area}} = \frac{2.4\text{g}}{\text{cm}^2}$

area = 4×2 cm² = 8 cm²

$2.4\,\text{g/cm}^2\,(8\,\text{cm}^2) = 19.2\,\text{g}$

sample weight =

$1.18\,\frac{\text{g}}{\text{cm}^3}\,(8)(.093) = .878\,\text{g}.$

0.24 g/g.

.5 mm.

23 hr

$$\frac{.24\,\text{gs}/.79\,\text{g/cm}^3}{\frac{.24}{.79} + 1/1.18} \quad \frac{.3}{.3+.85} = \frac{.3}{1.15} = 0.26 \text{ vol f}$$

Fig. 9. Experimental plots of weight increase per unit area and the front penetration parameters *l* and *d* against time for absorption of liquid methanol by PMMA at 30°C. The specimens were 40 mm × 20 mm × 0·93 mm thick and the equilibrium absorption was 24% w/w.[14]

and remained as such even though the methanol itself may subsequently desorb from the thin section. Optical densitometer scans across the sections (Fig. 10) showed the fronts, which were sharp to within the resolution of the optical microscope, and also the negligible concentration gradients behind them. Examination between crossed polars while sorption was taking place indicated that the swollen material had deformed by stretching in a direction normal to the front, in agreement with the original observations of Hartley.[6] This extension is understood as the consequence of swelling under conditions of area constraint, provided in this case by the unpenetrated glassy core.

The most simple defining characteristic of Case II sorption is the occurrence of a linear relationship between the mass of penetrant

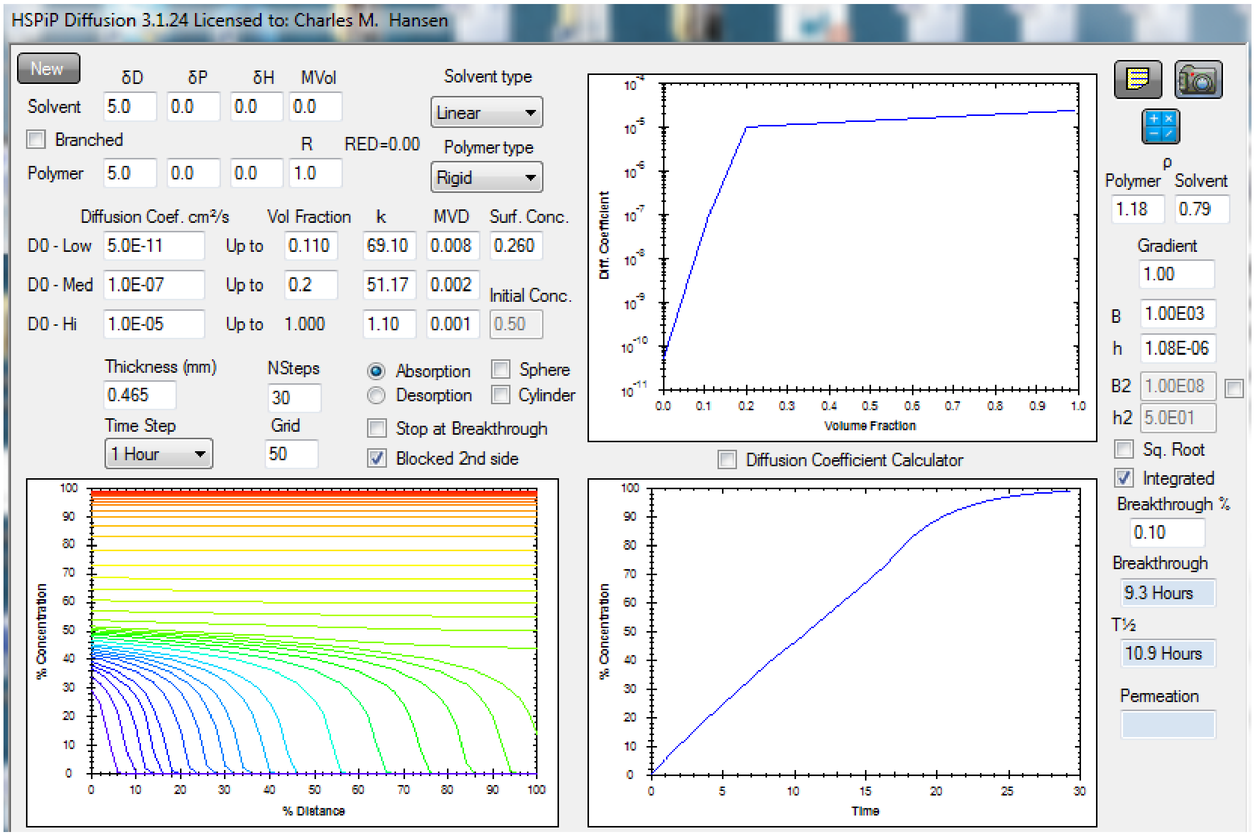
$$\left(1 + \frac{.93}{40} + \frac{.93}{20}\right)^2 = (1.06975)^2 = 1.14_4$$

This could/would obscure a slight delay at start.

Figure 2 (above). A copy of page 85 of reference [1] including some thoughts and calculations at first reading.

An alternate explanation for Case II absorption in polymers

The author has presented an alternate explanation for “anomalous” diffusion in polymers retaining sole use of the diffusion equation using exponentially concentration dependent diffusion coefficients and where required, a significant surface condition [8]. The derivation of the diffusion equation is very general and neglect of the surface condition would appear at this point in time as having been a major error in the relevant literature for many years [9]. A power point presentation including a discussion of these phenomena and alternate explanations for the results of Thomas and Windle experiments described here, as well as the experiments of Petropoulos and coworkers [11], can be downloaded from www.hansen-solubility.com.



HSPiP Diffusion 3.1.24 Licensed to: Charles M. Hansen

	δD	δP	δH	MVol
Solvent	5.0	0.0	0.0	0.0
				R
Polymer	5.0	0.0	0.0	1.0

☐ Branched

RED=0.00

Solvent type: Linear

Polymer type: Rigid

	Diffusion Coef. cm²/s		Vol Fraction	k	MVD	Surf. Conc.
D0 - Low	5.0E-11	Up to	0.110	69.10	0.008	0.260
D0 - Med	1.0E-07	Up to	0.2	51.17	0.002	Initial Conc.
D0 - Hi	1.0E-05	Up to	1.000	1.10	0.001	0.50

Thickness (mm): 0.465

NSteps: 30

Time Step: 1 Hour

Grid: 50

● Absorption ☐ Sphere

○ Desorption ☐ Cylinder

☐ Stop at Breakthrough

☑ Blocked 2nd side

☐ Diffusion Coefficient Calculator

ρ Polymer: 1.18 Solvent: 0.79

Gradient: 1.00

B: 1.00E03

h: 1.08E-06

B2: 1.00E08 ☐

h2: 5.0E01

☐ Sq. Root

☑ Integrated

Breakthrough %: 0.10

Breakthrough: 9.3 Hours

T½: 10.9 Hours

Permeation

Figure 3 uses data provided in Figures 1 and 2 for the absorption of methanol into PMMA at 30ºC. The linear uptake with linear time at the lower right reproduces the results in Figure 2. The methanol concentration gradients at the lower left are not sharp, advancing fronts. Methanol “fronts” meet at the center after about 9 hours compared with the data for iodine in Figure 1 where the “fronts” meet after about 23 hours. Step-like concentration gradients do not exist for methanol in this system according to this analysis based on the diffusion equation alone.

The concentration dependent diffusion coefficients estimated at the upper right in Figure 3 were used to generate the concentration gradients for methanol at the lower left in Figure 3, as well as the linear uptake curve with linear time at the lower right. The straight line uptake in Figure 3 duplicates the straight line found in Figure 2. The concentration gradients clearly do not duplicate what is given in Figure 1. The concentration gradients in Figure 3 are simply the result of solving the diffusion equation with the given parameters. The equilibrium concentration was 0.26 volume fraction methanol. A significant surface mass transfer coefficient, h, is required to duplicate the absorption curve. The assumed value for h is $1.08(10)^{-6}$ cm/s. The software used is available from www.hansen-solubility.com.

With regard to the estimated diffusion coefficients, one can expect an increase in the diffusion coefficients at low concentration in rigid polymers by a factor of 10 for a concentration increase of approximately 3 volume fraction. This statement is based on measurements for diffusion of smaller molecules in poly(vinylacetate) [12,13]. The diffusion coefficients and mass transfer coefficient were established after a number of trials that showed rather small changes in these resulted in rather large effects on the uptake curve. The self-diffusion coefficient for methanol is assumed at $2.4\ (10)^{-5}\ cm^2/s$ while the Do is taken as $5(10)^{-11}\ cm^2/s$. The assumed diffusion coefficient for pure methanol has no significant effect on the result, but is required to fully define the diffusion coefficients. The mass transfer coefficient reported in Figure 3, $1.08(10)^{-6}$ cm/s, cannot be considered as being precise, but is presumably not significantly in error. This value is not unreasonable when compared with similar values in other systems. A contributing reason for a mass transfer coefficient that apparently remains relatively constant is discussed below. A great deal of research remains to be done. The diffusion coefficients and entry mass transfer coefficient are presumably not accurate in any of these modeling results and should be confirmed by their experimental determination. Different combinations may give similar result. The general conclusions will remain the same, however.

The discussion in the following sections explains what has happened in the Thomas and Windle experiments in detail. The basis of the problem is that iodine is not a suitable tracer for following the concentration of methanol in the PMMA since it significantly lags methanol.

Iodine as an unsuitable tracer for methanol

The major problem with the experiments of Thomas and Windle is that the gradients within the samples were observed by adding an unsuitable tracer (iodine) to the methanol. The size of iodine is larger than that of methanol. The I-I bond is 270 pm with the radius of the iodine atom being 140 pm. Compare this with the minimum cross-sectional area of methanol, which is the "CH_3" group, as seen by rotating the 3D model in ChemSpider, for example. (*www.**chemspider**.com/Chemical-Structure.864.html*) The C-H bond length is 108.7 pm and this approximates the radius of the minimum cross section of the methanol molecule, a factor of some significance in diffusion. The iodine molecule can be thought of as two equally sized round balls attached to each other. The size of each of these balls is somewhat larger than the largest cross-section of the methanol molecule. The methanol molecule can be visualized as a dart with the preferred direction of diffusion in polymers being with the smaller alcohol group in advance of the larger methyl group.

The effect of molecular size can be seen in another chapter in *Polymer Permeability* (Comyn), this one written by Charles E. Rogers [14]. Figure 4 is reproduced from this chapter.

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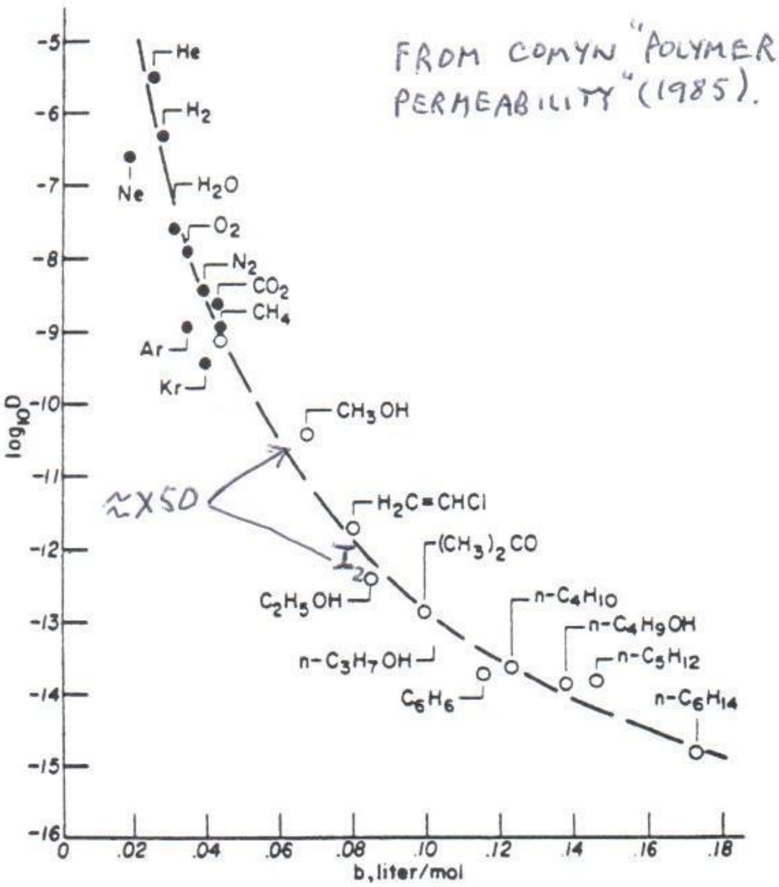

Fig. 12. Diffusivities of gases and vapours in poly(vinyl chloride) as a function of their van der Waals volume, *b*. (○) Data of Berens and Hopfenberg,[114] (●) data used by those authors from Tikhomirov *et al.*[128] (Reproduced, by permission, from ref. 114.)

Figure 4. The effect of molecular size on the diffusion coefficient at low concentration in poly(vinyl chloride). The diffusion coefficient of iodine is estimated to be clearly lower than that of methanol. It will also be lower than that of vinyl chloride by some margin. The diffusion coefficient of iodine in PMMA is estimated as being about 50 times lower than that of methanol in PMMA at very low concentrations as shown in the figure. This figure was reprinted from [14], but originated in [15].

The short story then is that the tracer iodine will always lag the methanol, and any precursor (the very front part of the advancing front) will not be seen because iodine has not gotten there.

What this analysis is saying is that the iodine is so far behind the methanol that it will indicate an essentially flat concentration gradient as shown in the Figure 1. The first insert in Figure 1 (Windle Figure 10) is for 13 hours, at which point the iodine has such a flat profile that has not penetrated the film yet. The methanol fronts have already met and the methanol concentration is essentially uniform in the whole film at about 60% of the saturation amount of methanol. The iodine will see a flat methanol profile at this point. The flat methanol concentration profiles slowly increase in concentration until the equilibrium amount is reached as can be seen in the lower left of Figure 3. The advancing front of methanol with the sharp drop-off in Figure 1 is a fiction according to this analysis. The iodine front happens to reach the center of the film at the same time as the film is saturated with methanol.

Further support for this conclusion is found by analyzing the data in Figure 1 to determine the local diffusion coefficients for iodine after 13 hours and after 18 hours of exposure.

Iodine diffusion coefficients in methanol-swollen PMMA

Approximate diffusion coefficients for iodine in methanol-swollen PMMA were evaluated by assuming that they are constant at the given condition. The calculations can be easily done for constant diffusion coefficients since $D_0t/(l)^2 = 1.0$ when 95% of saturation has been attained. See Crank, *Mathematics of Diffusion* (1957 corrected from 1956) Fig. 4.3 [16].

Using the data in Figure 1, which indeed are for iodine:

Time	Penetration Depth	Approximate Diffusion Coefficient
13 h.	0.296mm	1.87 E-08 cm^2/s
18 h.	0.38mm	2.23 E-06 cm^2/s

The local diffusion coefficients for methanol in methanol plasticized PMMA at these times/concentrations can be read from the computer screen, but not from its copies.

D(methanol) at 13 hours (about 0.15 volume fraction) is about $1(10)^{-6}$ cm^2/s as an average over the expected significant time interval.

The ratio of D(methanol)/D(iodine) is approximately 53 at this stage.

D(methanol) at 18 hours (about 0.21 volume fraction) is about $1(10)^{-5}$ cm^2/s as an average over the expected significant time interval.

The ratio D(methanol)/D(iodine) is approximately 4.3 at this stage.

It appears that the diffusion coefficient of iodine is about 50 times lower than that of methanol when both are present in PMMA at low concentrations. This is in agreement with the result using Figure 4 in the above where the diffusion coefficients pictured are those at essentially zero concentration in PVC. This same approximate relative behavior can also be expected in other polymers that can absorb the same chemicals. It is expected that this difference will become much smaller as the absorption process continues and higher methanol concentrations prevail. The difference will perhaps only be a factor of less than 2 for the pure components. The diffusion coefficient for iodine in methanol at 25ºC is given as $1.7(10)^{-5}$ cm^2/s in [17]. The difference in the diffusion coefficients of methanol and iodine decreases as the methanol concentration in the PMMA increases and the “sieving” effect of the polymer chains becomes less significant. This allows the iodine to “catch up” with the methanol such that the iodine front more or less coincides with the time at which the methanol concentration approaches its equilibrium value with an asymptotic tail of the type frequently seen in Case II absorption. That this happens at 30ºC is a matter of chance. It does not happen at higher temperatures and cannot be expected to happen at lower temperatures either. There is a considerable amount of estimation in this analysis, but the general picture is quite clear that the iodine is not a satisfactory tracer for methanol in polymeric systems. That this disparity is responsible for the illusion of step-like concentration gradients advancing linearly with time becomes still more evident in the following.

Molecular Orientation at Surfaces or “Why is there a Significant Surface Condition?”

The question of the nature of a significant surface question has been raised many times. This has been discussed in [8,12]. What might be called external factors for absorption include diffusion through a stagnant air layer, supply to the surface from a distant source, and removal of heat from the film to allow further condensation. These are generally associated with rather high diffusion coefficients in the polymer that remove the diffusing material to the bulk faster than it can get through the surface. With liquid contact the main effects appear to be the adsorption of the chemical on the polymer surface, it subsequent orientation and location of a suitable entry site (not a polymer segment), and then diffusion through the surface layer. The larger the molecule, or perhaps more importantly, its maximum cross-sectional area, the lower will be the entry mass transfer coefficient. The entry mass transfer coefficient, generally associated with liquid contact, can be orders of magnitude lower than that generally associated with vapor or gas contact. When molecules become too large, they simply cannot pass through the surface, and the entry mass transfer coefficient, heretofore also indicated (perhaps unfortunately) with “h” is zero. This situation allows for major effects based on the size of the diffusing molecules and the entry mass transfer coefficient can vary over many decades from zero and upwards. This has been discussed in [8].

One aspect of this entry phenomenon that this study has brought out more clearly is that Nature continually tries to keep the surface free energy at a minimum. For polymers this leads to reduction of the surface free energy of the polymer/air surface by preferential location of low energy species oriented toward the air. In general these surface entities are hydrocarbon species, while the functional groups are then buried with orientation towards the bulk. Polymer chain segment rotation can take place when there is contact with given liquids. With long term exposure to water, for example, a surface which initially rejected water in the form of droplets or film retraction can become one which readily allows spontaneous spreading or retains water films.

When PMMA is exposed to methanol the CH_3 group of the methanol will preferentially orient toward the polymer surface where the hydrocarbon nature has been emphasized as discussed above. There is very little affinity for the alcohol group. This effect can make entry of methanol into PMMA more difficult than would otherwise be suspected, since the alcohol group has very little affinity for a hydrocarbon entity. In addition to this the chemical structure of methanol can be likened to that of a dart as stated above. (*www.**chemspider**.com/Chemical-Structure.864.html*). The direction of preferential diffusion of methanol in a polymer is given by this structure with the smaller alcohol group leading the way in preference to the larger CH_3. Since the preferred direction of adsorption onto the polymer surface is the reverse of this, the methanol molecule will have more difficulty adsorbing onto the PMMA surface in such a way as to most easily diffuse into the bulk. There will be a surface entry effect that is thought to be the primary cause of the significant surface condition in the methanol/PMMA system. The physical entry of the methanol molecule requires the lodging of the alcohol group into a suitable receptor/hole in the PMMA surface which is in no way partial to this orientation. When a given methanol molecule does succeed in entering the bulk, the polymer surface will tend to go back to where it was before, with the CH_3 groups of the methanol in the bulk liquid again preferentially oriented toward a low energy polymer surface. This effect may largely explain why the mass transfer coefficient appears to be constant to a first approximation, even though the bulk concentration of solvent increases.

Additional support for a special surface layer on the PMMA surface is found in [7] and given here in Table 1. While Windle would prefer to explain this in terms of stress, it offers a clue as to why there is a surface condition of significance altogether.

Cooling rate through T_g, ºC/s	Induction time, h	Time for front to penetrate 1 mm at initial rate, h
13.3	1.2	58
1.7	1.8	91
0.025	3.5	135
0.01	5.0	160

Table 1. Induction times for methanol sorption at 24ºC for samples of different thermal history

The samples used in Table 1 were annealed for 1 hour at 130ºC as were all of the other samples examined for absorption rates other than these. The explanation offered here for these results is that an induction time is intimately connected with the surface and hence the surface condition in terms of the entry mass transfer coefficient. The slower the cooling rate the more easily the

PMMA can develop a lower energy surface enriched with hydrocarbon entities. Likewise the packing will be closer, with lower free volume, such that not only is the orientation of the methanol affected by these phenomena, but the diffusion coefficient likewise will be greatly reduced. There is ample reason to predicate an entry surface resistance as being responsible for the Case II model given in Figure 3 and in the Super Case II behavior shown below.

Super Case II

Super Case II is characterized by an increasing rate of uptake with linear time. The absorption of methanol into PMMA at 0ºC is given in Figure 23 of [1], taken from [5], as an example of Super Case II absorption. Figure 4 is a copy of the page where this appears in [1].

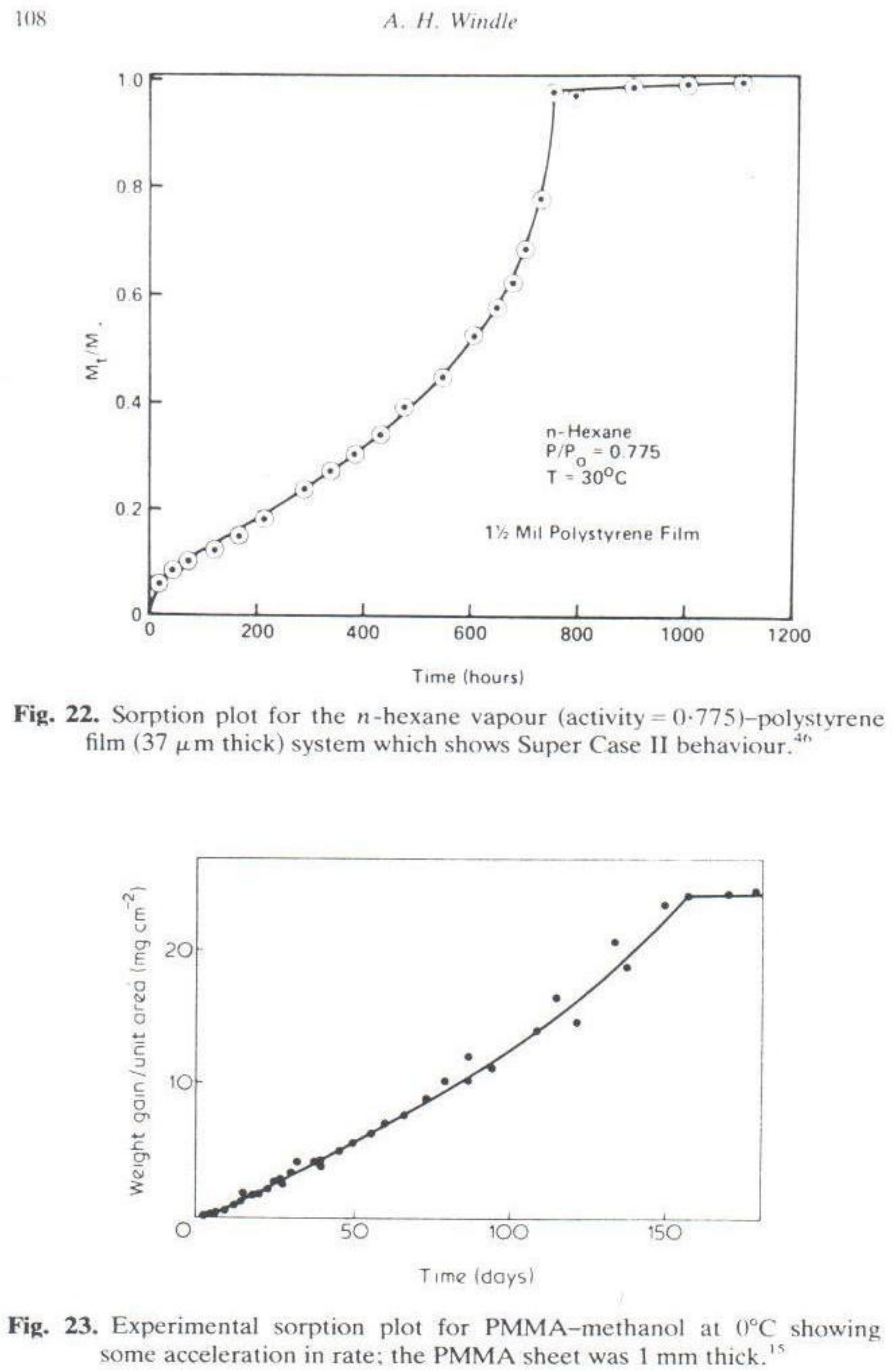

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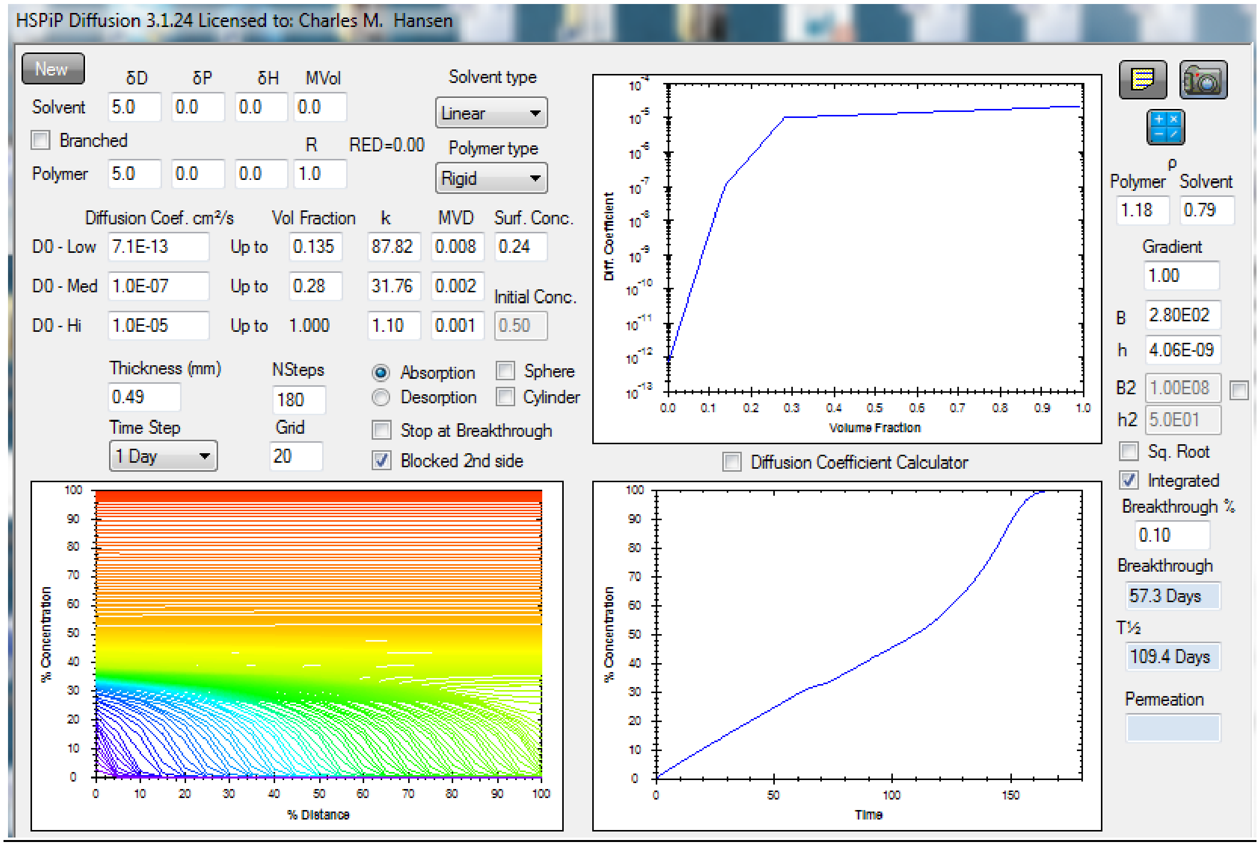
Fig. 22. Sorption plot for the *n*-hexane vapour (activity = 0·775)–polystyrene film (37 μm thick) system which shows Super Case II behaviour.[46]

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 4. Copy of page 108 in [1] showing two cases of Super Case II absorption. Figure 5 models the absorption of methanol in PMMA at 0ºC is given in Figure 23 of [1], taken from [5].

There is some scatter in the figure for methanol in PMMA, but there is a clear trend for an increased uptake rate during the experiment. Figure 5 below replicates the essential features of the experiment and the time at which equilibrium appears to have been reached. Many attempts to achieve a smoother increase in the rate did not give any improvement over that presented, which, however, could well be encompassed by the scatter in the data. The more pronounced upward curvature at the latter stage of the experiment is also seen in the data for the absorption of n-hexane in polystyrene in Figure 4 that is an excellent example of Super Case II taken from [18]. The presence of some end effects of significance in the 1 mm samples as discussed below may also be a problem in attaining a perfect match. There may also be an induction time to consider as discussed above. An induction time slowing the uptake would counteract any significant end effects that increase the initial uptake rate. It is concluded that Super Case II as given in [5] for the absorption of methanol into PMMA at 0ºC is suitably matched here for the sake of demonstrating the ability of the diffusion equation alone to model the experiment. The trends are the same as for the Case II data with the methanol meeting in the middle of the free film after about 57 days after which the concentration profiles stabilize with an essentially uniform methanol concentration in the film that slowly rises at an increasing rate with time until the equilibrium is reached. There are no advancing fronts. There is an indication of the typical asymptotic tail at the very last stage. This asymptotic tail can also be seen in the data for the absorption of n-hexane into polystyrene found in [18] and given in Figure 4. No concentration gradients have been reported for this experiment, so the iodine lag behind the methanol has not been established. This is not considered significant since it has been established for the data at 30ºC above and at 62ºC in the following.

The conclusion of this discussion is that the Super Case II data in [1,5] for the absorption of methanol into PMMA at 0ºC are well matched by the solving the diffusion equation with concentration dependent diffusion coefficients and a significant surface condition.


HSPiP Diffusion 3.1.24 Licensed to: Charles M. Hansen

	δD	δP	δH	MVol
Solvent	5.0	0.0	0.0	0.0
Polymer	5.0	0.0	0.0	R 1.0

☐ Branched

RED=0.00

Solvent type: Linear

Polymer type: Rigid

	Diffusion Coef. cm²/s		Vol Fraction	k	MVD	Surf. Conc.
D0 - Low	7.1E-13	Up to	0.135	87.82	0.008	0.24
D0 - Med	1.0E-07	Up to	0.28	31.76	0.002	Initial Conc.
D0 - Hi	1.0E-05	Up to	1.000	1.10	0.001	0.50

Thickness (mm): 0.49

NSteps: 180

Time Step: 1 Day

Grid: 20

● Absorption ○ Desorption ☐ Sphere ☐ Cylinder

☐ Stop at Breakthrough

☑ Blocked 2nd side

☐ Diffusion Coefficient Calculator

ρ Polymer: 1.18 Solvent: 0.79

Gradient: 1.00

B: 2.80E02

h: 4.06E-09

B2: 1.00E08 ☐

h2: 5.0E01

☐ Sq. Root

☑ Integrated

Breakthrough %: 0.10

Breakthrough: 57.3 Days

T½: 109.4 Days

Permeation:

Figure 5 simulates absorption of methanol into PMMA at 0ºC as reported in [1,5]. The absorption curve bends upwards with time and ends at about 160 days. The small blip at about 70 days in the calculations is a result of the fronts meeting in the middle of the film, and until the essentially flat concentration profile in the whole film is established at higher concentrations of methanol. This result can be fitted into the spread of data reported in Figure 4 for this experiment.

Effects of higher temperature

Changes in temperature can be expected to change both the diffusion coefficients and the mass transfer coefficients, and the relative effects will determine the final result. The diffusion coefficients and the mass transfer coefficients that produce Super Case II have been shown to be lower than those that produce Case II [2].

This is also seen when comparing the data in Figure 3 with the data in Figure 5. D_0 decreases from $5(10)^{-11}$ cm^2/s to $7.1(10)^{-13}$ cm^2/s when the temperature falls from 30ºC to 0ºC, with the entry mass transfer coefficient decreasing from $1.08(10)^{-6}$ cm/s to $4.06(10)^{-9}$ cm/s for the same temperature difference. It would be expected that the absorption of methanol into PMMA at higher temperatures will progress more rapidly, and with a higher surface mass transfer coefficient. The overall effect is an approach to what are called Fickian kinetics as found by

Thomas and Windle for absorption of methanol into PMMA at higher temperatures [4]. Data for the absorption of methanol into PMMA at 62ºC are given in Figure 6 reproduced from [4].

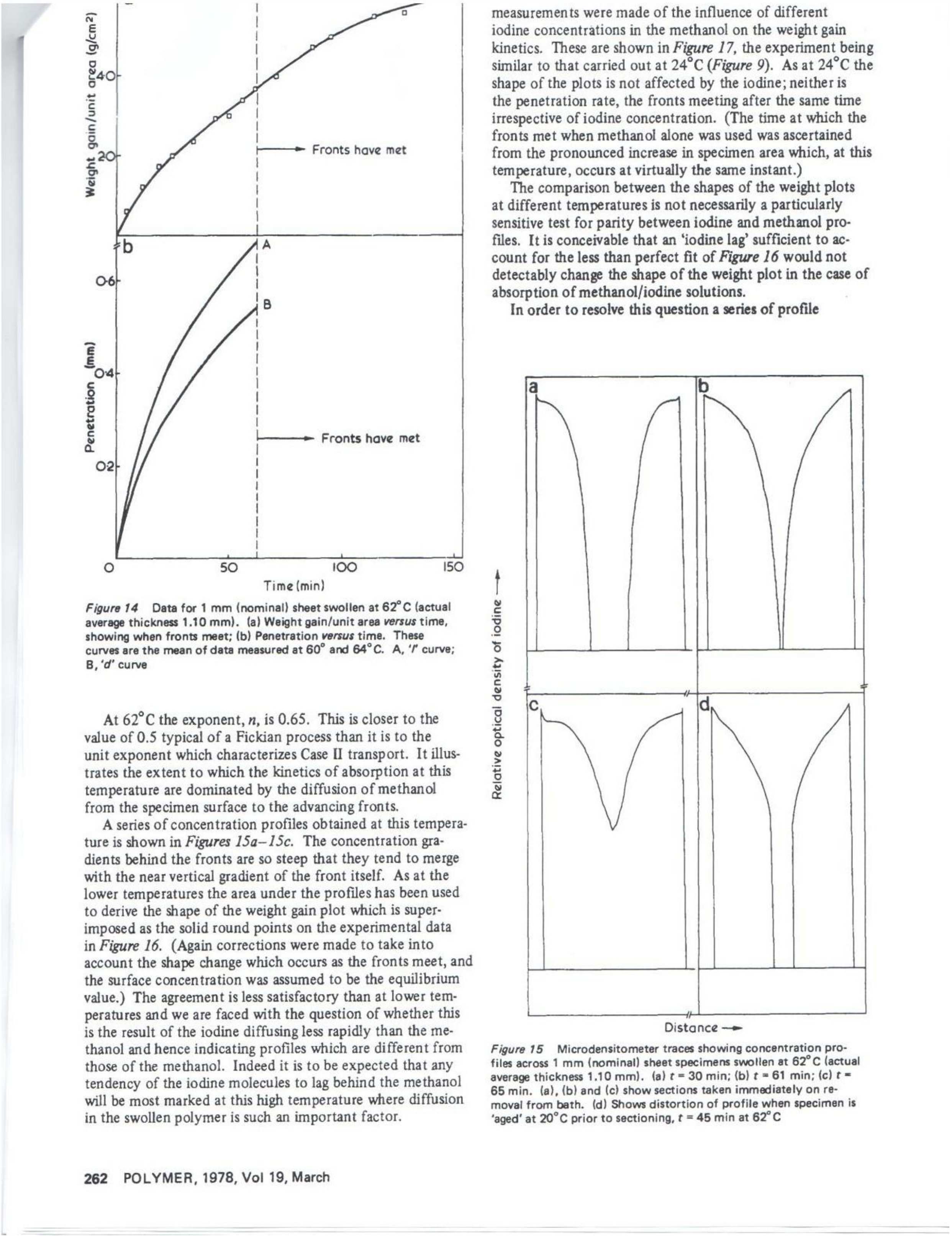


Figure 14 Data for 1 mm (nominal) sheet swollen at 62°C (actual average thickness 1.10 mm). (a) Weight gain/unit area *versus* time, showing when fronts meet; (b) Penetration *versus* time. These curves are the mean of data measured at 60° and 64°C. A, '*l*' curve; B, '*d*' curve

At 62°C the exponent, *n*, is 0.65. This is closer to the value of 0.5 typical of a Fickian process than it is to the unit exponent which characterizes Case II transport. It illustrates the extent to which the kinetics of absorption at this temperature are dominated by the diffusion of methanol from the specimen surface to the advancing fronts.

A series of concentration profiles obtained at this temperature is shown in *Figures 15a–15c*. The concentration gradients behind the fronts are so steep that they tend to merge with the near vertical gradient of the front itself. As at the lower temperatures the area under the profiles has been used to derive the shape of the weight gain plot which is superimposed as the solid round points on the experimental data in *Figure 16*. (Again corrections were made to take into account the shape change which occurs as the fronts meet, and the surface concentration was assumed to be the equilibrium value.) The agreement is less satisfactory than at lower temperatures and we are faced with the question of whether this is the result of the iodine diffusing less rapidly than the methanol and hence indicating profiles which are different from those of the methanol. Indeed it is to be expected that any tendency of the iodine molecules to lag behind the methanol will be most marked at this high temperature where diffusion in the swollen polymer is such an important factor.

measurements were made of the influence of different iodine concentrations in the methanol on the weight gain kinetics. These are shown in *Figure 17*, the experiment being similar to that carried out at 24°C (*Figure 9*). As at 24°C the shape of the plots is not affected by the iodine; neither is the penetration rate, the fronts meeting after the same time irrespective of iodine concentration. (The time at which the fronts met when methanol alone was used was ascertained from the pronounced increase in specimen area which, at this temperature, occurs at virtually the same instant.)

The comparison between the shapes of the weight plots at different temperatures is not necessarily a particularly sensitive test for parity between iodine and methanol profiles. It is conceivable that an 'iodine lag' sufficient to account for the less than perfect fit of *Figure 16* would not detectably change the shape of the weight plot in the case of absorption of methanol/iodine solutions.

In order to resolve this question a series of profile

Figure 15 Microdensitometer traces showing concentration profiles across 1 mm (nominal) sheet specimens swollen at 62°C (actual average thickness 1.10 mm). (a) *t* = 30 min; (b) *t* = 61 min; (c) *t* = 65 min. (a), (b) and (c) show sections taken immediately on removal from bath. (d) Shows distortion of profile when specimen is 'aged' at 20°C prior to sectioning, *t* = 45 min at 62°C

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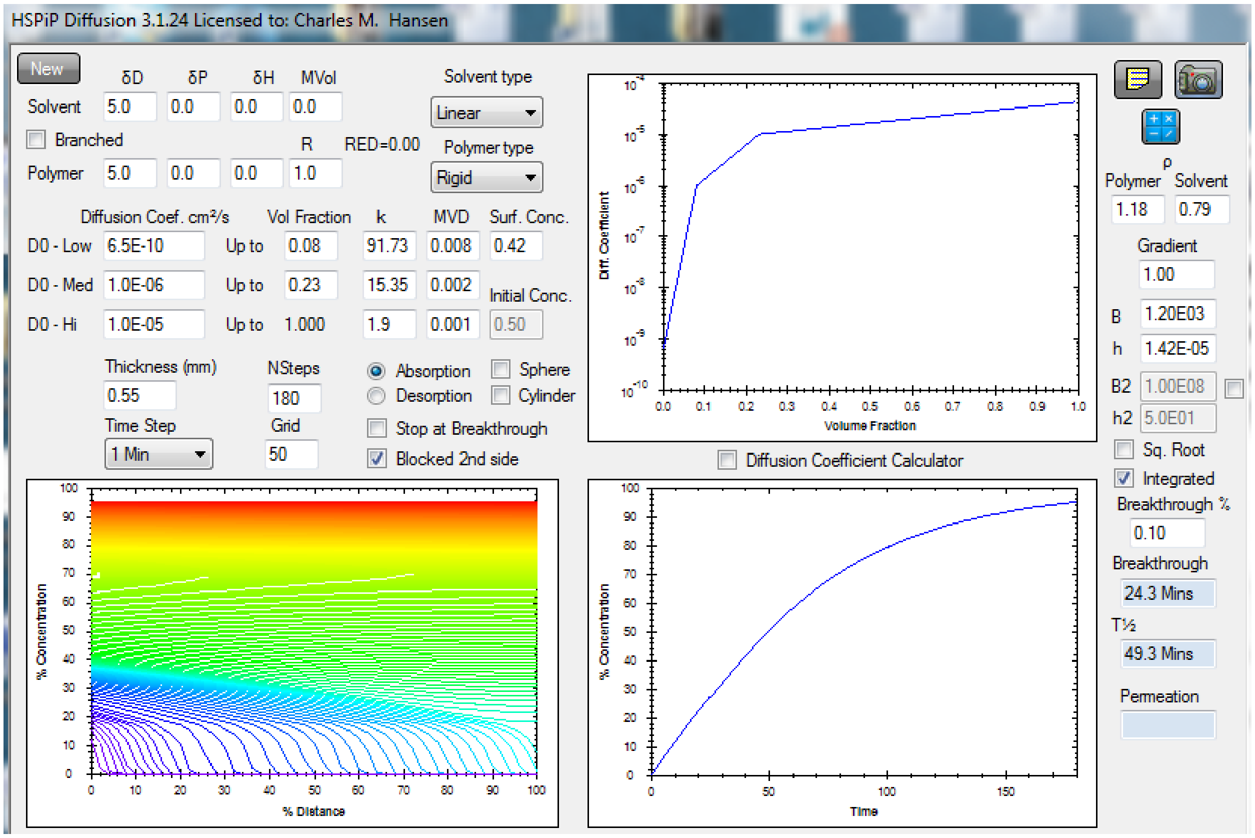
Figure 6. Absorption of methanol into PMMA at 62ºC. From [4].



HSPiP Diffusion 3.1.24 Licensed to: Charles M. Hansen

	δD	δP	δH	MVol
Solvent	5.0	0.0	0.0	0.0
Polymer	5.0	0.0	0.0	R 1.0

☐ Branched

RED=0.00

Solvent type: Linear

Polymer type: Rigid

	Diffusion Coef. cm²/s	Vol Fraction		k	MVD
D0 - Low	6.5E-10	Up to	0.08	91.73	0.008
D0 - Med	1.0E-06	Up to	0.23	15.35	0.002
D0 - Hi	1.0E-05	Up to	1.000	1.9	0.001

Surf. Conc. 0.42

Initial Conc. 0.50

Thickness (mm) 0.55

NSteps 180

Time Step 1 Min

Grid 50

● Absorption ☐ Sphere

○ Desorption ☐ Cylinder

☐ Stop at Breakthrough

☑ Blocked 2nd side

☐ Diffusion Coefficient Calculator

ρ Polymer 1.18 Solvent 0.79

Gradient 1.00

B 1.20E03

h 1.42E-05

B2 1.00E08 ☐

h2 5.0E01

☐ Sq. Root

☑ Integrated

Breakthrough % 0.10

Breakthrough 24.3 Mins

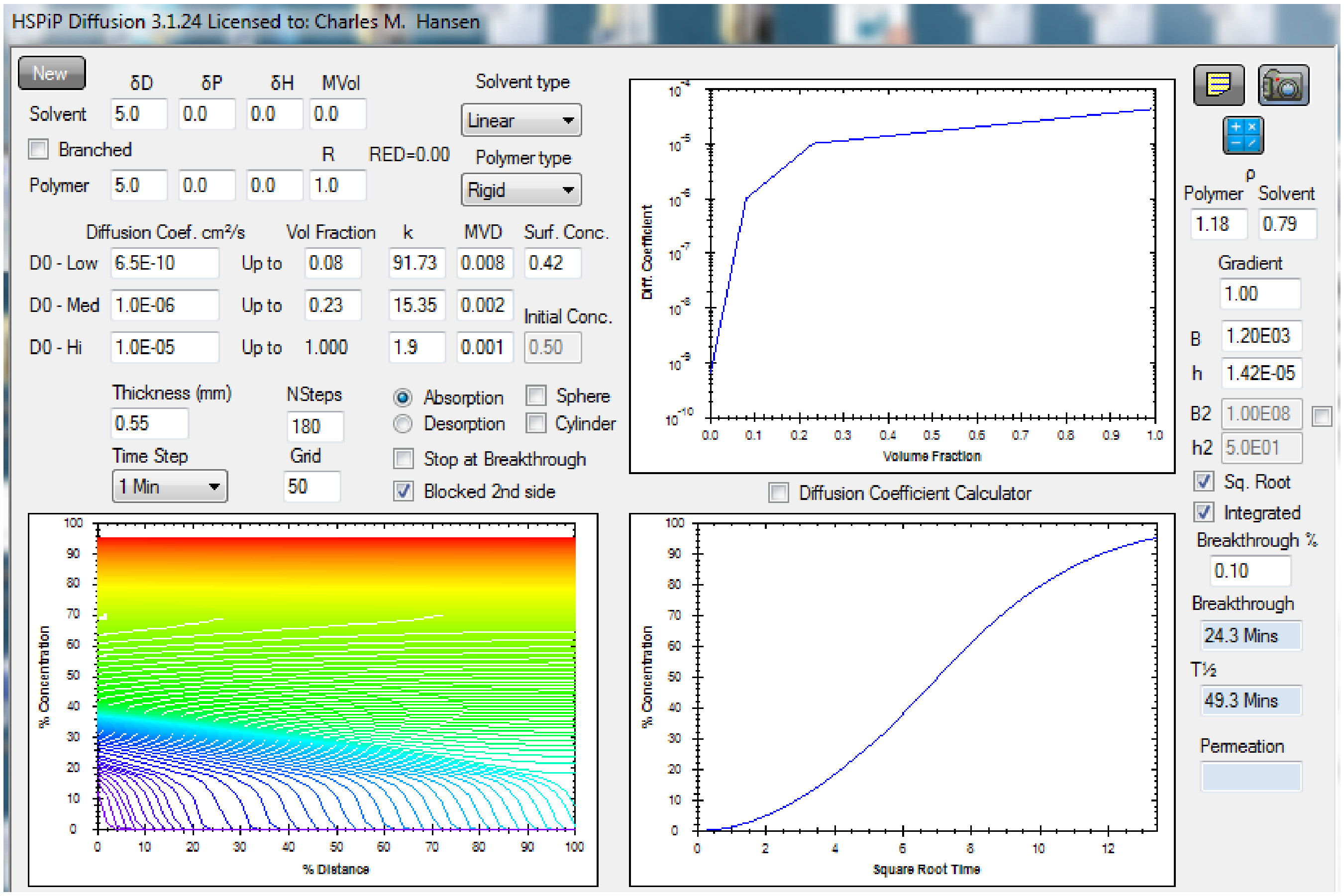
T½ 49.3 Mins

Permeation

Figure 7. Modeling of the absorption of methanol into PMMA at 62°C using data from [4].

The features of the absorption curve in Figure 6 (upper left) are essentially the same as those reported in Figure 7 (lower right). The general picture again is that the methanol "fronts" meet before the iodine fronts in this case after only 24 minutes. The fronts for the iodine tracer meet after about 60 minutes. The iodine is lagging the methanol. The representation of the methanol absorption using iodine is in error. This possibility was recognized in [4], but dismissed for other reasons. These were the (continued) assumption of parity between the diffusion of iodine and methanol and problems of handling samples taken at the higher temperature allowing methanol evaporation before being "fixed" for the profile analysis. The entry mass transfer coefficient, $1.47(10)^{-5}$ cm/s, is higher than in the other cases discussed above as is the diffusion coefficient at essentially zero concentration, $6.5(10)^{-10}$ cm^2/s. The diffusion coefficient for pure methanol was increased to $4.3(10)^{-5}$ cm^2/s. The diffusion coefficients assumed as a function of concentration cannot be considered precise, but are believed to be approximately correct since the absorption curve is matched rather well.

It is concluded that the diffusion equation can model the absorption of methanol into PMMA at 62°C where the characteristics are somewhere between what is called Case II and what is called Fickian. Figure 8 confirms that these same data modeled with the same parameters as in Figure 7 gives what is called a sigmoidal or S-shaped absorption curve when the square root of time is used in the absorption curve.



HSPiP Diffusion 3.1.24 Licensed to: Charles M. Hansen

	δD	δP	δH	MVol
Solvent	5.0	0.0	0.0	0.0
Polymer	5.0	0.0	0.0	R 1.0

☐ Branched

RED=0.00

Solvent type: Linear

Polymer type: Rigid

	Diffusion Coef. cm²/s		Vol Fraction	k	MVD	Surf. Conc.
D0 - Low	6.5E-10	Up to	0.08	91.73	0.008	0.42
D0 - Med	1.0E-06	Up to	0.23	15.35	0.002	Initial Conc.
D0 - Hi	1.0E-05	Up to	1.000	1.9	0.001	0.50

Thickness (mm): 0.55

NSteps: 180

Time Step: 1 Min

Grid: 50

● Absorption

○ Desorption

☐ Sphere

☐ Cylinder

☐ Stop at Breakthrough

☑ Blocked 2nd side

☐ Diffusion Coefficient Calculator

ρ Polymer: 1.18

ρ Solvent: 0.79

Gradient: 1.00

B: 1.20E03

h: 1.42E-05

B2: 1.00E08 ☐

h2: 5.0E01

☑ Sq. Root

☑ Integrated

Breakthrough %: 0.10

Breakthrough: 24.3 Mins

T½: 49.3 Mins

Permeation:

Figure 8. Modeling absorption of methanol into PMMA at 62ºC using the square root of time plot to show sigmoidal or S-shaped absorption. This type of uptake curve has also traditionally been called non-Fickian or anomalous, but the diffusion equation is fully capable of reproducing the experimental data.

The diffusion of iodine is lagging that of methanol in these data at 62ºC as can be seen from the time at which the "fronts" meet for iodine being about 61 minutes versus about 24 minutes for methanol. The diffusion coefficient for methanol is estimated as above at $1(10)^{-5}$ cm^2/s for the time at which the iodine fronts meet at the center of the film, with the diffusion coefficient for iodine at this time being about $8.27(10)^{-7}$ cm^2/s. The iodine lags the methanol by a factor of about 12. It is shown again that iodine is not a good tracer for methanol in this system.

Thickness effects on absorption

The effect of an increase in thickness is that surface phenomena become less significant relative to the diffusion in the bulk. A thick film may therefore not demonstrate Case II absorption, for example, while a thinner film will for the same experimental conditions. Likewise a thicker film showing linear uptake with the square root of time many show S-shaped uptake for a thinner film. The effect of film thickness is easily accounted for with the procedure outlined in the above. There are insufficient data to examine this effect in the present system, especially since edge effects can become more significant as film thickness increases.

Edge effects

There is a very complete treatment of edge effects in [6]. It is concluded in [6] that these do not significantly affect the reported results. It would be rather complicated to fully account for these effects in the present modeling when the surface condition is also a dominant effect. The variation in the film thicknesses around the nominal 1 mm in the various experiments performed by Thomas and Windle is probably more significant than this effect, but a synergistic combination of the two could, of course, become significant. An estimate of the significance of edge effects can be gotten from a treatment based on the initial uptake for a constant diffusion coefficient given in [19]. The apparent diffusion coefficients, D_{app}, vary from the true value, D_{true}, according to the following equation:

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

L is the thickness of a free film, l is its length, and w is its width. For the film thickness of 0.93 mm for the experiment examined in Figure 1, the difference is a factor of 1.14 according to this equation, but again, this is not directly applicable when there is concentration dependence and/or when there is a significant surface condition.

Discussion

Berens and Hopfenberg report a diffusion coefficient for methanol in PMMA at low concentration at 30ºC [15]. This value $1.6(10)^{-11}$ cm^2/s compares well with the value used in Figure 3 where D_0 ended at $5(10)^{-11}$ cm^2/s after numerous tries to finally match the absorption curve. The agreement is satisfactory in view of potential differences between practices and samples from different laboratories. Reasonable curve fitting was also possible by slightly adjusting several of the parameters with a forced D_0 equal to $3(10)^{-11}$ cm^2/s, but the general picture is not changed and the original attempt that appeared better is maintained. The agreement is presumed to be better than the numbers above indicate when it is recognized that the diffusion coefficients included in [15] did not account for a significant surface condition. The present analysis confirms that there will be a significant surface condition for all thicknesses less than about 1mm (actually much greater) at all reasonable temperatures, and it is doubtful that thicker films were used for this purpose in [15]. When the transport process is slowed at the surface by a significant surface condition, and this is not accounted for, the (apparent) diffusion coefficient that is found will be too low.

The experiments of Petropoulos and coworkers [see 11, also for further references] have been reinterpreted by this same simple approach that does not require consideration of stress relaxation. The most relevant results of this explanation are found at the last of a power point presentation on diffusion in polymers that can be downloaded from www.hansen-solubility.com.

The main results of this report are also included in the same power point presentation for the sake of completeness.

The chemistry of iodine can be rather complicated depending on the system. Thomas and Windle have evaluated this in the present system and found no problems in its use as a tracer in methanol for reasons of its reaction potential [4]. It is expected to be a good solvent for PMMA by analogy with bromine and its gelling behavior with PMMA in concentrated solutions [4]. Iodine molecules are expected therefore to diffuse as individual molecular entities and therefore could have been a good tracer for methanol if diffusion coefficients had been close to those of methanol, which they are not as shown above.

The Thomas and Windle studies have been used to examine the diffusion of methanol in PMMA since the necessary data were all present for numerous cases. These papers have excellent discussions of important phenomena, but whenever the interpretation is based on the results obtained with the iodine tracer, the interpretations are not in agreement with what is presented here. There appears to be no need to consider a theory based on relaxation as a major controlling effect. Solutions to the diffusion equation have been shown to model the uptake curves satisfactorily. In addition to this major disagreement related to the theory, there are several other points that would seem to need more careful consideration. One of these is estimation of the activation energy for the diffusion process. It is not the purpose of this paper to focus on the excellent discussions of end effects [4] and three dimensional swelling [6], or mechanical properties [7], however.

The rate of movement of the advancing “front” is not thought to be a good quantity with which to evaluate activation energies as has been done in [4]. The activation energy found in [4], for methanol penetration for constant concentration at the fronts was found to be 25 kcal/mol. This is discussed in [4] as being too high by comparison with other systems. A better rate parameter would have been the diffusion coefficient, but diffusion coefficients are not reported anywhere in the Thomas and Windle publications. The slope of the weight gain curve would not appear to be a completely reliable value for this purpose for several reasons. The iodine tracer technique is not measuring the methanol concentration at the fronts. That the surface condition is a very significant part of determining the rate of uptake since the surface concentration only slowly rises as the absorption process proceeds. The slope of the absorption curve is therefore the result of a composite effect of the surface condition as well as highly concentration dependent diffusion coefficients at a variety of concentrations. It is not surprising that the activation energy found in the experiments is higher than expected when passage of the surface is much more difficult than normally expected. The special nature of the surface of the PMMA has been exposed by the results in [7] as discussed in the following.

The effect of different cooling rates through the glass transition temperature after prolonged annealing at 130ºC were studied in [7]. This cooling rate imposes a very significant effect on the absorption of methanol into PMMA at 24ºC. There is a significant time lag (induction time) that increases as the cooling rate becomes slower. These data are interpreted as showing the development of a PMMA surface that has an orientation more in harmony with the reduction of the surface free energy as the cooling rate decreases. There is also less free volume slowing diffusion not only in/through the surface itself, but also in the bulk. The reported induction times vary in a uniform manner from 1.2 hours for the cooling rate used in the majority of the experiments, 13.3ºC/s, to 5.0 hours when the cooling is reduced to 0.01ºC/s. The time for the front to penetrate 1 mm at the initial rate is also reported as 58 hours and 160 hours, respectively, for these two cases. This is interpreted here as the development of a surface that is less amenable to passage when the cooling rate is very slow, since this allows a closer packing of the oriented PMMA molecules.

Summary

This document confirms that the suitable solutions to the diffusion equation itself successfully model what are commonly called “anomalies” of diffusion (absorption) in polymers. These include absorption curves that demonstrate a delay or time-lag when data are plotted using the square root of time (S-shaped or sigmoidal), or linear uptake with linear time (Case II), or uptake with an increasing rate with linear time (Super Case II). This has also been demonstrated in the past [8], but the data of Thomas and Windle and Windle [1-7] are so extensive and well presented as to warrant a very close look at this alternative explanation.

The experiments of Thomas and Windle have been cited many times as typical examples of what is called Case II absorption [1,3]. The explanations of “anomalous” diffusion offered by them as well as by Petropoulos and coworkers [11 and references therein] involve stress relaxation phenomena. The simple approach used by the author to model diffusion in polymers in general uses only the diffusion equation coupled with, if necessary, exponentially concentration dependent diffusion coefficients and/or a significant surface condition. This provides a more general alternate explanation of the various phenomena dealt with in diffusion in polymers including absorption with or without the so-called “anomalies”, desorption including film formation from solution, and permeation, as through chemical protective gloves [8,20].

The Thomas and Windle data discussed here lead one to believe methanol absorption into PMMA is a typical example of Case II taking place with a methanol front advancing linearly with time, and with a step-like concentration profile. It is shown that the diffusion of iodine is far too slow to reliably reflect the diffusion of methanol in the relevant experiments. The uptake is indeed linear with time, but there is no advancing, sharp front for the methanol. The tracer iodine cannot detect this and the methanol “fronts” based on iodine tracer experiments shown in various figures are misleading. At 30ºC the “fronts” for methanol would meet at about 9 hours compared with the iodine fronts used to model them that meet at about 23 hours. There is no step-like advancing concentration profile for the absorption of methanol into PMMA at 0ºC, 30ºC, or 62ºC. The fact that the iodine fronts coincide with the end of the uptake curve for methanol is a matter of chance occurring at 30ºC. This does not occur at 62ºC, for example.

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