

Response to the Criticism of Petropoulos and Coworkers

The following is excerpted from a manuscript that was rejected by the European Polymer Journal. It should be read in context with my other related documents on the validity of the diffusion equation for explaining all aspects of diffusion in polymers. No changes in the numbers for the equations, figures, or references have been made here. I have tried to incorporate this in abbreviated form into two subsequent manuscripts without success. This is put on my website since the full details given here are important for those who wish to delve more deeply into the discussion “What Controls “Anomalous” Diffusion in Polymers – Stress Relaxation in the Bulk or a Significant Surface Condition in the Diffusion Equation?”

Excerpts follow:

How can the two explanations model the experiments so well?

A stress relaxation interpretation has somehow allowed a reasonable match for the absorption curve of water vapor into poly(vinyl alcohol). How can this happen? The answer to this is as follows. The stress control approach uses a “kinetic” modulus, $\beta L^2/D$. According to [3], D/L^2 , the diffusion coefficient divided by the film thickness squared, governs the diffusion rate, and β is the rate parameter (“relaxation frequency” = reciprocal relaxation time) of a swelling volume relaxation process described by

$$\partial C/\partial t = \beta(C^{eq} - C) \quad (1)$$

C^{eq} is the final concentration and C is a local concentration, which for moderate values or high values such as in [2] would approximate the surface concentration, C_s . Diffusion within the film is so rapid as to essentially equalize the concentration in the film. There are no concentration gradients of significance in the experiments reported in [2] after about 10% of the solvent is absorbed as can be seen in Fig. 2 of [1]. So C_s is also essentially equal to the bulk concentration for the majority of the absorption process. The right hand side of Eq. (1) therefore gives the mass transport (flux) through the surface. The equation predicts an exponential rise in the concentration with time.

The modulus used by Petropoulos et al is very closely related to the dimensionless surface condition modulus used by Crank [10] and Hansen, (hL/D_0) , for conditions at the surface only

$$\alpha \text{ (Crank)} = h \text{ (Hansen)} \quad \text{and}$$

$$B \text{ (Hansen)} = hL/D_0 \text{ (Hansen)} = l\alpha/D \text{ (Crank)} = L \text{ (Crank)}$$

At the absorbing surface the flux F_s , toward the interior of the film, given by Fick’s First Law, is equal to the flux from the external media to/through the surface:

$$F_s = -D\partial C_s/\partial t = h(C^{eq} - C_s) \quad (2)$$

By assuming various values for the either the kinetic stress control modulus or Cranks surface condition modulus one can find absorption curves essentially identical to those given by Crank [10] showing the sigmoidal or S-shaped absorption curves.

In the nomenclature used in [3], β could be replaced by α/l (h/L) or the reverse, α (or h) could be replaced by β (adjusted by the film thickness) and the calculated results will be very close. The interpretation is then up to the individual as to which mechanism is the correct one since Eqs. (1) and (2) can produce absorption curves that can be indistinguishable from each other. See also the discussion below.

The following is a quote from [3] regarding the work presented in Tamura et al [15].

Quote:

“ Accordingly a study of Stage II absorption enabled Tamura et al [Ref. 28 in 3] to report viscous swelling kinetics practically *coincident* with those exhibited by parallel mechanical tensile creep experiments; thus unmistakably pointing to a swelling relaxation process having a *common* physical origin with that governing mechanical creep (and excluding potential alternative interpretations e.g. in terms proposed in [10,11].”

End of quote.

The references [10,11] in the quote are references [16,1, respectively] in this document (both to Hansen).

One is led by the above quote to believe that Tamura et al [15] actually performed Stage II absorption experiments that paralleled a mechanical study. In fact this was not done.

Tamura et al [15] studied tensile creep in atactic polystyrene that had been saturated in advance to given equilibrium amounts with benzene at two temperatures (25°C and 35°C). Retardation (relaxation) times for use in a mechanical (Voight) model for stress relaxation are reported. There are no absorption experiments. There is no report of viscous swelling kinetics.

The experiments reported by Tamura et al [15] were all done at concentrations low enough so the system was below the glass transition temperature, but the results have been applied to the second stage of absorption where the concentrations would be somewhat higher, and presumably above the concentration giving a glass transition temperature. This is true for the data presented in [2] as an example. The consensus of researchers at that time was that stress relaxation was a viable explanation for the second stage of the absorption curves, that is, where the concentrations are highest.

Quoting from Tamura et al [15]:

“Recently, Long and Richman⁵⁾ have shown that the two-stage absorption curves can be derived from Fick diffusion equation with the concept of variable surface concentration. They expressed the dependence of surface concentration, c_1^s , on time by the following equation: $c_1^s = c_1^i + (c_1^\infty - c_1^i)[1 - \exp(-\beta t)]$. Here, c_1^i is the concentration at the quasi-equilibrium and is only a small fraction of the final equilibrium value c_1^∞ , and β is a rate parameter.”

Long and Richman find that:

“These results, though yet of a preliminary nature, may give clear evidence that the second portion of the two-stage absorption is primarily caused by slow rearrangements of polymer network chains.”

Tamura et al [15] find a correlation between the measured mean retardation times and the concentrations at which they were measured and there also is a correlation with $1/\beta$. This is interpreted by Petropoulos and coworkers as proof positive of the stress relaxation mechanism at much higher concentrations in the second stage. The Long and Richman article above is cited in [1] as reference [15], and here as [17], because it presented the possibility that both the prevailing stress relaxation mechanism and an exponential increase in the surface concentration could correlate the two-stage absorption behavior. That this latter proposal could be the case can also be seen in Crank [18] where several two stage curves are calculated for different rates of exponential increase of the surface concentration. A significant mass transfer coefficient leads to an exponential increase in the surface concentration, in agreement with the possibility expressed by Long and Richman. This was not recognized at the time, however. The β (retardation times) could in principle equally well have been used to estimate the exponentially rising surface concentration and resulting absorption.

In view of the following excerpt from [3], it appears necessary to discuss still another example. It is stated in [3] that

“Another useful feature of this experimental approach here is that Hansen’s postulated surface resistance [11] is rendered ineffective (since penetration across the film is prevented by the glass plates).”

The reasoning behind this statement should have been explained in more detail.

Petropoulos and coworkers have done a special experiment with stretched cellulose acetate films in the thickness range of 90-110 microns that are sandwiched between two glass plates and then exposed to liquid dichloromethane. The experiment is described in Fig. (8) of [3] and the accompanying text as well as in [22]. The arrangement allows for diffusion in the direction of the orientation as well as perpendicular thereto into the film. The clamped glass plates (microscope slides) prohibit motion other than in the two directions parallel to the glass plates. One direction is designated as along the direction of stretching with the other as being across the direction of stretching. As stated in [22], it is well known that the properties of stressed polymers are

somewhat weaker in the direction perpendicular to the direction of the orientation than they are in the stretched direction. The stretching can be assumed to establish a permanent new structure in the cellulose acetate film, with the rigid, rod-like, cellulose acetate polymer chains assuming a different orientation with multiple physical bonds to neighboring polymer molecules. Prior to stretching the chains are more or less randomly oriented, crudely modeled by a pile of sticks.

Fig. (2) models the above experiment for diffusion in the direction across that of the direction of orientation/stretching. The concentration gradients are identical to those in Fig. (8c) in [3] and closely resemble those in Crank for concentration diffusion into a semi-infinite medium [23], where the diffusion coefficient varies exponentially by a factor between 95 and 200 over the concentration range of interest. The exponential change in the diffusion coefficient was taken as 125 in the Fig. (2) with the diffusion coefficient at very low concentration, D_0 , being $8(10)^{-9}$ cm^2/s . The concentration at the exposed surface was 0.26 volume (0.36 g/g) corresponding to that reported in connection with the experiment. It is also reported that this is reduced from the normal measured equilibrium amount 0.73 volume fraction (2.8g/g) because of the constraints of the glass plates. Diffusion coefficients are included at the upper right in Fig. (2) for concentrations higher than 0.26 volume fraction, but these are not used in the calculation. They are required by the modeler. The diffusion coefficient for the pure solvent should in reality not exceed that of its self-diffusion. The total distance in Fig. (2) at the lower right is 1mm. The computation was stopped just before the advancing front reached this point to compare with the data in Fig. (8a) in [3]. There is complete agreement. Diffusion in this direction can therefore be modeled perfectly with a concentration dependent diffusion coefficient as given in Fig. (2). There is no significant surface effect here and neither does any stress related factor appear necessary since simple exponential concentration dependent diffusion coefficients are all that is necessary.

The diffusion into the stretched cellulose acetate in the direction of orientation is much slower than across it. The reason for this could be that moving a polymer molecule, or significant segment thereof, is required for diffusion to occur. Cellulose from wood pulp has typical chain lengths between 300 and 1700 glucose units. The polymer chains are very stiff. It would be reasonable to assume that many of these would have associated many times with neighboring molecules in the stretching direction, whereas much fewer of such “physical bonds” would be found in the perpendicular direction. It much easier to move the long, stiff molecules in the “across” direction, and diffusion of molecules whose size resemble that of a glucose unit need not go so deeply into the bulk before significant polymer segment motion is possible. In the stretched direction a much larger number of solvent molecules must enter the polymer in order to provide appropriate polymer mobility for significant diffusion. The required depth of penetration of solvent is only a few “glucose units” in the across direction to provide the concentration dependent diffusion. The “distance” in the direction of orientation may be as much as several hundred “glucose units” before a cellulose molecule is “freed” sufficiently to allow very rapid diffusion at very much higher concentrations behind the advancing front. There must be

appreciable uptake of solvent before the polymer chains can move suitably. When this is achieved, the motion will be dramatic because the concentration is so high just behind the moving front. This process can continue with successive polymer molecules being “freed”, and the front moves through the film. This physical model then allows for a very high diffusion rate behind a very sharp advancing front as seen in Fig. (8c) in [3]. A stress relaxation interpretation would not agree with this model, but with the adjustable parameters in the modeling procedure of Petropoulos and coworkers, it does simulate the uptake curve very well, while the concentration gradients show a sharp front, but with too rapid advancement of what is called the precursor [3]. The diffusion coefficients are not reported which somewhat reduces the ability to fully evaluate the stress relaxation model. The reason for the precursor being too dramatic is that the (unreported) diffusion coefficient(s) at low concentrations are too high. It may also be that the diffusion coefficients at the highest concentration are too high in comparison with the expected self-diffusion coefficient of dichloromethane. Higher diffusion coefficients at the higher concentrations enhance the supply of solvent to the advancing front and give a sharper curvature downward there.

Fig. (3) shows how the modeler in [12] can be set up to confirm that the description of diffusion in the direction of orientation given above is basically correct. The diffusion coefficient is assumed constant at $2(10)^{-13}$ cm²/s at concentrations less than 0.05 volume fraction. Above this concentration there is an exponential increase in two steps to a maximum value of the diffusion coefficient equal to $1(10)^{-5}$ cm²/s. This is a little under what one might expect for the self-diffusion coefficient of dichloromethane. The surface concentration is again 0.26 volume fraction. There is a moderately significant surface mass transport coefficient attributed to difficulty in entering the oriented polymer at the surface. This leads to the two stage absorption curve. The surface effect is no longer significant when the absorption curve becomes a straight line on the uptake plot at the lower right in the figure. The absorption curve in Fig. (3) matches that reported in Fig. (8a) in [3]. The concentration gradients clearly show an advancing front, although not as sharp at the top, as that in Fig. (8c) in [3]. In view of the simple modeling approach, this is judged satisfactory to demonstrate the viability of the physical model discussed above. A more refined diffusion coefficient profile, especially at higher concentrations, could possibly improve the match, but this is felt beyond present needs. It may also be that the concentration of dichloromethane behind the front is (locally) higher than that assumed for the equilibrium in the restrained, stretched state. This would lead to higher diffusion coefficients at the higher concentrations and to a sharper front.

Finally, it might be added that data are presented for exponential diffusion coefficients that are analyzed in defensible ways in [1, 24] for diffusion of four solvents in poly(vinylacetate), and by Crank [25] for the diffusion of chloroform in poly(styrene). Both of these support the choice of D_0 used in Fig (3). Extrapolating Crank’s data to zero concentration yields a diffusion coefficient, D_0 , equal to, or very near, that used in Fig. (3), this being $2(10)^{-13}$ cm²/s.

Conclusion

The β used by Petropoulos and coworkers as a rate parameter for stress relaxation with a “kinetic” stress relaxation modulus can also describe the rate of exponential increase of the surface concentration during absorption to higher solvent concentrations as suggested by Long and Richman [17]. Eqs. (1) used by Petropoulos and coworkers and (2) used by Hansen give essentially identical results for given conditions, if not completely so, with β (adjusted for film thickness) approximating a mass transfer coefficient, h , or vice versa depending on one’s viewpoint. β is included in the “kinetic” modulus used by Petropoulos and coworkers for modeling absorption in polymers at any prevailing concentration, even those at conditions well above the glass transition temperature of the system for vapor absorption into viscous liquids at high concentrations. A surface mass transfer coefficient is included in the modulus B as used by Hansen (L in the notation of Crank). Experiments have shown that this can be significant not only for absorption, but also for desorption including film drying from solution concentrations normally used in the coating industry. Likewise even steady state permeation experiments, such as measured in permeation cells by the protective clothing industry and other cases as discussed above and in [1], demonstrate a need for the surface condition in solutions to the diffusion equation to properly model experimental data. The surface concentration is sometimes not immediately at the equilibrium value, and in other situations it never even reaches the equilibrium value. It would appear impossible for a “kinetic” stress relaxation modulus to model steady state permeation with the surface concentration not reaching the equilibrium value while the approach of Hansen can do this readily. The surface mass transfer coefficient can normally be measured in the laboratory or found by curve fitting. Several examples of the results of Petropoulos and coworkers, previously interpreted on a stress relaxation model, have been modeled satisfactorily with diffusion coefficients exponentially dependent on concentration of the solvent, using a significant mass transfer coefficient in the surface condition for solving the diffusion equation where necessary. Significant surface mass transfer coefficients can arise from at least two distinct and separate effects, but these can be modeled with the same mathematics. The first is for external effects for experiments usually involving a vapor phase where the coefficient is relatively large. The second is for larger molecules that find entry into and through the polymer surface relatively difficult. Here the surface entry coefficient is very much lower, and has even been demonstrated to be zero in several cases where expected solvents simply could not pass through the surface because their molecules were too large.

REFERENCES

1. 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.
2. Hasimi A Stavropoulou A Papadokostaki KG Sanopoulou M. Transport of water in polyvinyl alcohol films: effect of thermal treatment and chemical crosslinking. *Eur Polym J* 2008;44:4098-4107.

3. Petropoulos JH Sanopoulou M Papadokostaki KG. Physically insightful modeling of non-Fickian kinetic energy regimes encountered in fundamental studies of isothermal sorption of swelling agents in polymeric media. *Eur Polym J* 2011;47:2053-2062.
4. Hansen CM. Doctoral Dissertation: The three dimensional solubility parameter and solvent diffusion coefficient, their importance in surface coating formulation. Copenhagen: Danish Technical Press; 1967. Can be downloaded free from www.hansen-solubility.com.
5. Hansen CM Diffusion coefficient measurements by solvent absorption in concentrated polymer solutions. *J Appl Poly Sci* 1981;26:3311-3315.
6. Hansen CM. Hansen solubility parameters: a user's handbook. 2nd ed. Boca Raton FL: CRC Press; 2007. [Chap. 16].
7. Hansen CM. Organic solvents in high solids and water-reducible coatings. *Prog Org. Coatings* 1982;10:331-352.
8. Holten-Andersen J Hansen CM. Solvent and water evaporation from coatings. *Prog. Org. Coatings* 1983;11(3):219-240.
9. Perry's Chemical Engineering Handbook, 4th Ed., Perry JH. Ed. New York:McGraw Hill; 1963 [p. 14-26].
10. Crank J. The mathematics of diffusion. Oxford: Oxford University Press; 1956 [p. 57].
11. Hansen CM. A mathematical description of film drying by solvent evaporation. *J Oil Colour Chemists' Assn* 1968;51(1):27-43.
12. Abbott S Hansen CM Yamamoto H. Hansen solubility parameters in practice: Complete with software, data and examples. Hoersholm Denmark: www.hansen-solubility.com; 3rd ed. 2010. ISBN -978-0-9551220-2-6.
13. Kim SN, Kammermeyer K. Actual concentration profiles in membrane permeation. *Sep Sci* 1970;5(6):679-97.
14. Hwang S-T, Kammermeyer K. Effect of thickness on permeability. In: Hopfenberg HB, editor. Permeability of plastic films and coatings. New York: Plenum Press; 1974. p. 197-205.
15. Tamura M Yamada K Odani J. Tensile creep measurement on the system polystyrene and benzene. *Rep Prog Polym Phys Japan* 1963;6:163-6.
16. Diffusion in polymers. *Poly Eng Sci* 1980;20(4):252-258.
17. Long FA Richman D. Concentration gradients for diffusion of vapors in glassy polymers and their relation to time dependent diffusion phenomena. *J Am Chem Soc* 1960;82(3):513-519.

18. Crank J. The mathematics of diffusion. Oxford: Oxford University Press; 1956 [p. 50].
19. Nielsen TB Hansen CM. Significance of surface resistance in absorption by polymers. Ind Eng Chem Res 2005;44(11):3959-3965.
20. Skaarup K. Abstract, Lecture at Nordic Polymer Days, 1988.
21. Skaarup K. Report: Grænseflademodstand ved diffusionsprocesser i polymerer, Danmarks Ingeniør Akademi, Kemiafdeling (in Danish) 1981. (Translation: Surface resistance in diffusion processes in polymers)
22. Petropoulos JH Sanopoulou M. Test of a model of stress-dependent diffusion by means of combined colored tracer and birefringence profile measurements. J Polym Sci Part B:Polym Phys 1988;26:1087-99.
23. Crank J. The mathematics of diffusion. Oxford: Oxford University Press; 1956 [p. 270].
24. Hansen CM. Hansen solubility parameters: a user's handbook. 2nd ed. Boca Raton FL: CRC Press; 2007. [p.244].
25. Crank J. The mathematics of diffusion. Oxford: Oxford University Press; 1956 [p. 244].
26. Kiil S. Quantification of simultaneous solvent evaporation and chemical curing in thermoset coatings. J Coat Technol Res 2010;7(5):569-586.
27. Cairncross RA, Durning CJ. A model for drying of viscoelastic polymer coatings. AIChE J September 1996;42(9);2415-2425.
28. Crank J. The mathematics of diffusion. Oxford: Oxford University Press; 1956 [pp. 242-246].

Texts for Figures

Fig. 1. Fig. (1) models absorption with estimated, but realistic concentration dependent diffusion coefficients (upper right), and an estimated, realistic significant mass transfer coefficient. The advancing front concentration gradients are shown at the lower left. The upward curvature on the plot of uptake versus linear time (lower right) is characteristic for what is called Super Case II behavior. Fig. (3) shows that advancing fronts can also be found for what appears to be Case II behavior.

The following may be deleted or included in the text to the figure:

Solutions to the diffusion equation, such as shown in the figure, are usually presented in terms of relative absorption (or desorption) with the amount going from 0 to 1, or as a percentage of the equilibrium amount, on a basis of dry polymer film. The resulting plots for concentration gradients are given in terms of dry polymer. This means a thicker film would be observed in the laboratory than that directly read from the plots. The observed thickness will differ from the plotted thickness to a greater extent nearer the surface where absorption is taking place. This should be recognized when viewing calculated concentration gradients and enhances the appearance of an advancing front.

Fig. 2. Fig- (2) models absorption into a restricted, stretched cellulose acetate film in contact with liquid dichloromethane perpendicular to the direction of orientation. The film is sandwiched between two glass microscope slides and is stretched in one direction as described in [3,22]. The concentration gradients given in Fig. (8c) of [3] for diffusion perpendicular to the direction of orientation for this experiment are matched in the lower left of this figure. See also the gradients presented by Crank that likewise match this shape [23]. The experimental time for the front to reach 0.8 mm is about $t^{1/2}$ equal to 9.5, which is equally matched by the curve at the lower right in the figure. The diffusion coefficients used to match these conditions are given in the upper right in the figure. The equilibrium concentration is 0.26 volume fraction. There is no significant surface mass transfer coefficient. The value of h used in the figure is not necessarily the right one, having arbitrarily been set too high to have significance.

Fig. 3. Figure 3 models absorption of dichloromethane into an oriented cellulose acetate film in the direction of orientation. The diffusion coefficients are assumed to be constant at $2(10)^{-13}$ cm^2/s at concentrations less than 0.05 volume fraction. Above this concentration there is an exponential increase to $2(10)^{-6}$ cm^2/s at the surface concentration equal to 0.26 volume fraction. There is then an exponential rise to an assumed value for the pure dichloromethane at $1(10)^{-5}$ cm^2/s . There is a moderately significant surface mass transport coefficient equal to $2(10)^{-6}$ cm/s that leads to the two stage absorption curve. The absorption curve here matches the curve reported in Fig. (8a) in [3]. The concentration gradients clearly show an advancing front, although not as sharp as that in Fig. (8c) in [3]. In view of the simple modeling approach, this is judged satisfactory to demonstrate the viability of the physical model discussed in the text.

Figure 1 (below)

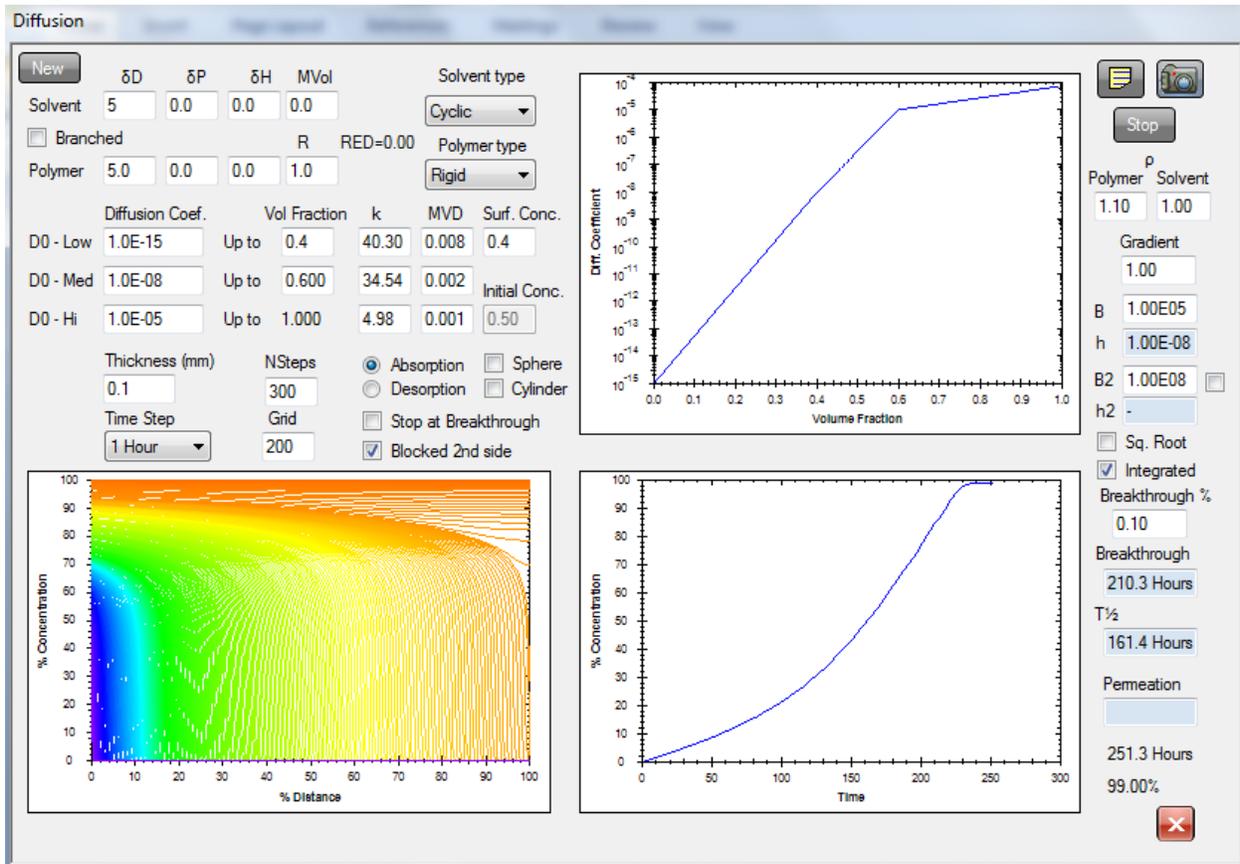


Figure 1 (above)

Figure 2 (below)

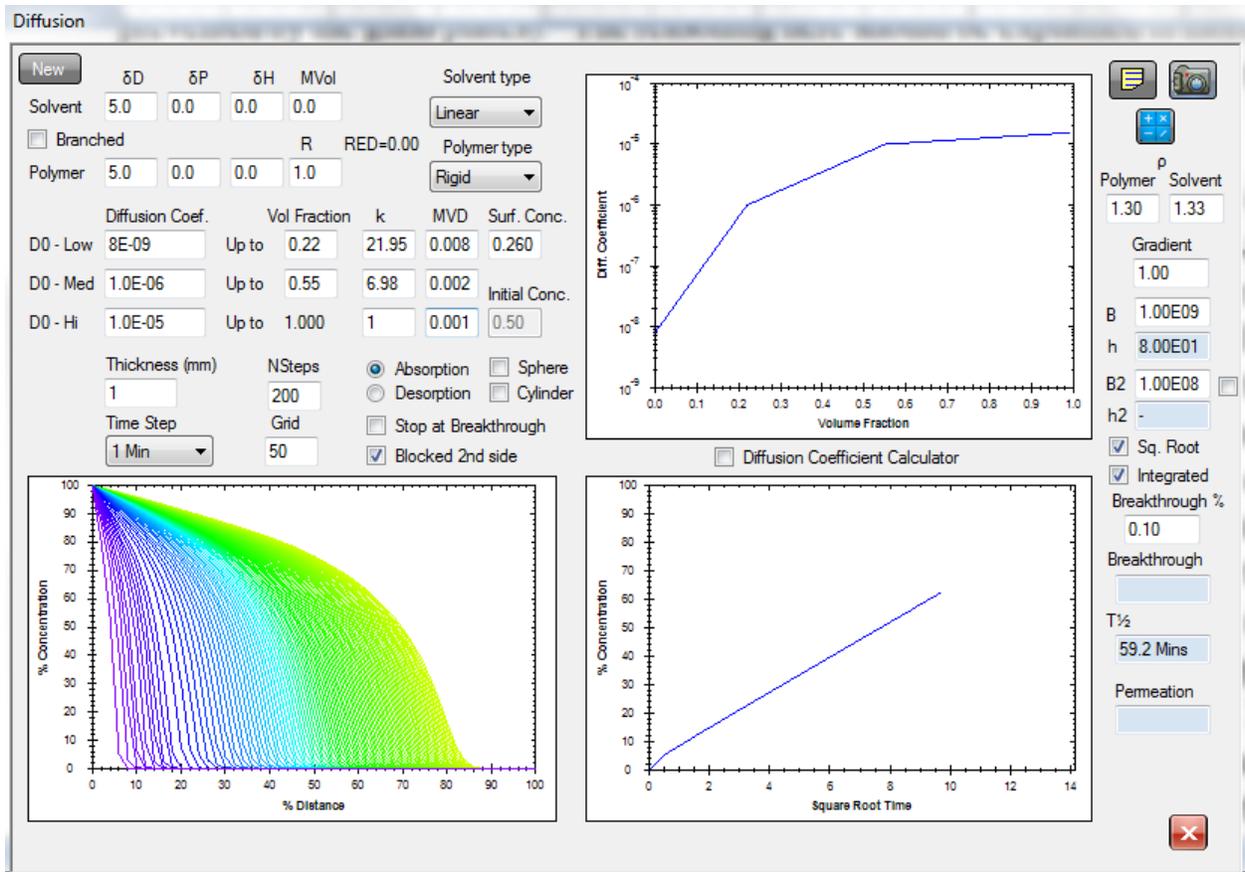


Figure 2 (above)

Figure 3 (below)

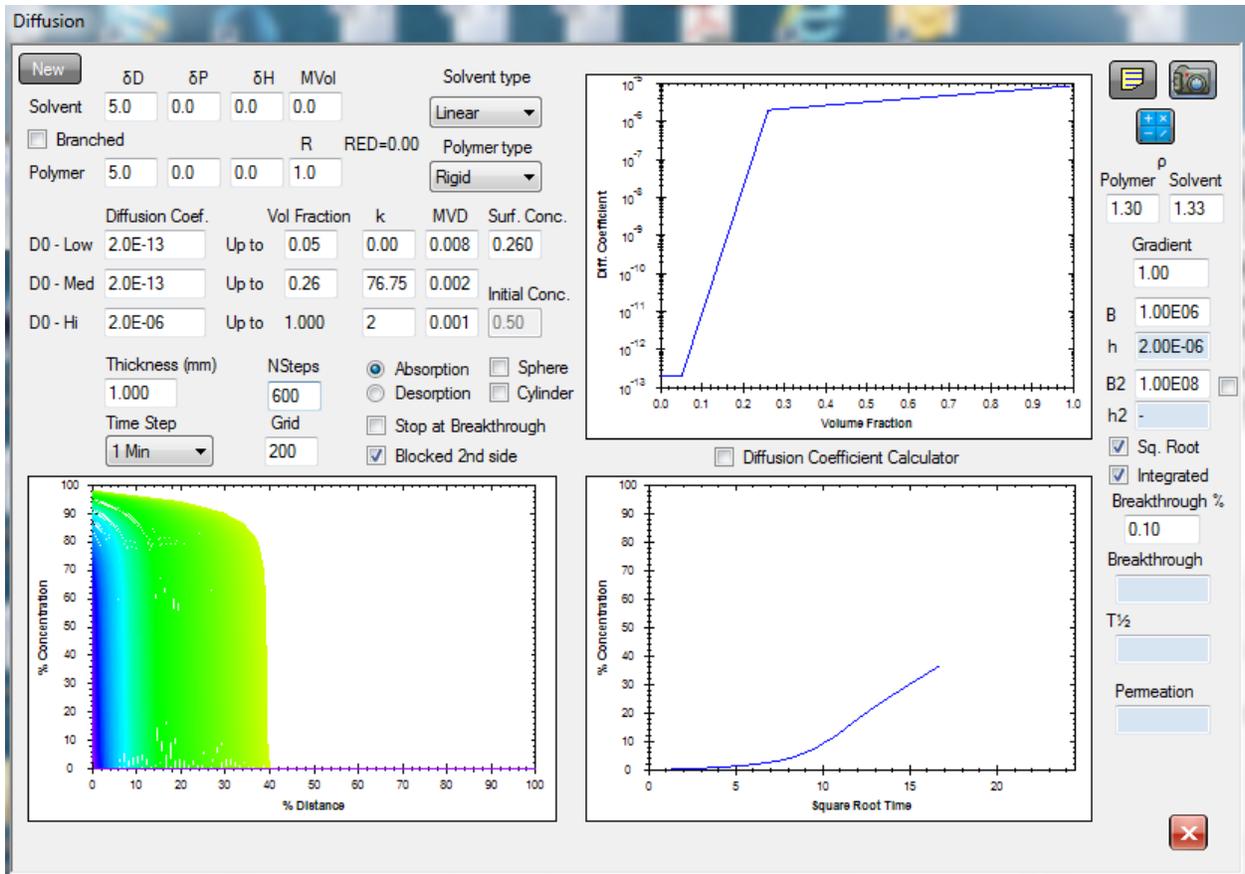


Figure 3 above