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The Rate of Solvent Diffusion in Amorphous Polymers

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SUMMARY: The present work is a contribution to our understanding of one aspect of the diffusion process, the diffusion rate. It attempts to show that all diffusion theories must satisfy the following:
1) the rate of diffusion at the initial stages of the process must be finite
2) the rate of diffusion must have square root time dependence at longer diffusion distances.
Deviations of experimental data from these rules usually result from experimental inaccuracies. Whereas Fickian approach satisfies the second but not the first rule and Case II sorption the opposite, their combination satisfies neither. Two alternative explanations, which provide a very good correlation with the experimental data, are suggested: limited diffusion rate and sorption kinetics.

Introduction

Permeability to liquids and gases together with mechanical properties are the most important properties of polymeric materials and for this reason most extensively studied. In order to control and predict these properties, the mechanism and the important parameters must be known. Most often the rate of weight gain is measured and a Fickian mechanism is assumed. This process can be conveniently described by one parameter, the diffusion coefficient D. It is also assumed that the diffusion rate is slowing down with square root time. The Fickian theory was derived in 1855 1) on the assumption that the transport of molecules follows the same principle as the transfer of kinetic energy of molecular vibration (heat) and is thus concentration driven. It had however been recognised as early as 1939 2) that the concentration profile does not correlate with this mechanism and numerous corrections 3-5) and new mechanisms 6-8)

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have been proposed. In the present work the diffusion rates, as predicted by different theories are discussed and correlated with new experimental data.

The diffusion front

In classical Fickian diffusion the rate of diffusion is described by a *diffusion coefficient* D. For a planar interface the concentration is changing with time t and distance x as $c=c_0$ erfc $(x/2(Dt)^{1/2})$. The definition of a diffusion front is arbitrary and it can be conveniently chosen for a concentration $c=0.1573\ c_0$ which satisfies $c= c_0$ erfc(1), or $x=x_0= 2(Dt)^{1/2}$, where x_0 is the *diffusion distance* (Figure 1). This can be written as $x_0=Bt^{1/2}$, where B is the *diffusion constant.*

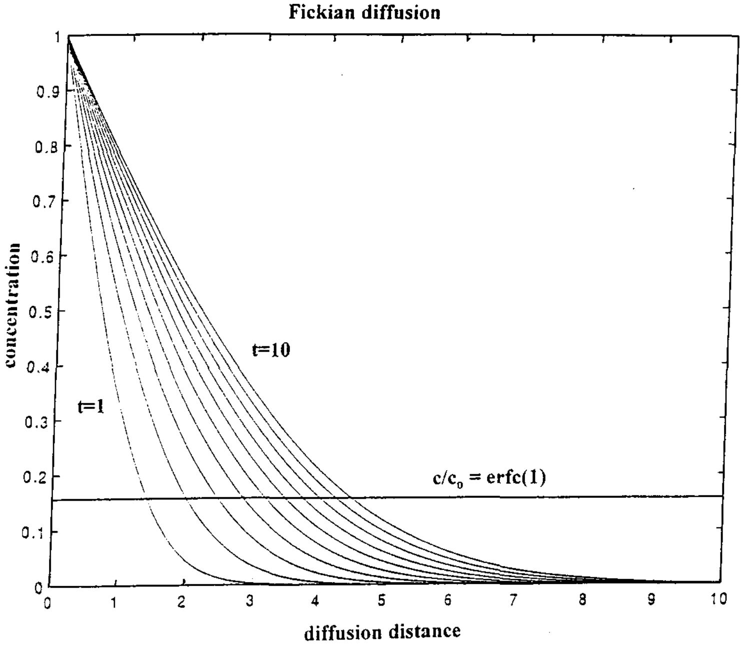

Figure 1. Fickian concentration profile. The diffusion front is defined for erfc(1)

For non-Fickian diffusion, which is almost exclusively observed, the calculated concentration profile is shown in Figure 2. The observed diffusion front is very sharp and thus easy to measure. The definition of the diffusion front in this case is the inflection point in the transient from concentration c_0 to zero concentration. The contrast between two regions with different refractive indexes (the swollen region is partially oriented) is sufficiently strong for obtaining accurate measurements with the aid of an image analyser[9].

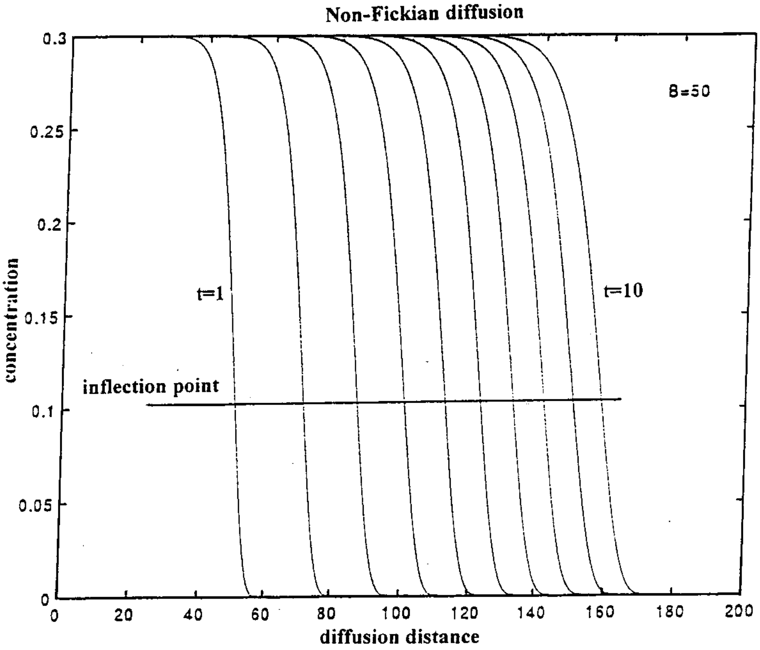

Figure 2. Non-Fickian concentration profile. The diffusion front is defined for the inflection point.

The measured data of time dependence of the diffusion distances for methanol in poly(methyl methacrylate) (PMMA) at room temperature (23°C) are shown in Figure 3. Swelling has not been subtracted from the total diffusion distance, but this will only change a numerical value, which is of no interest in this work.

The time dependence of the diffusion distance, x_0 has been measured for a large number of polymer-penetrant systems and is reported in the literature as $x_0=Bt$, $x_0=Bt^{1/2}$ or as their mixture. None of these models fits the experimental data too well over the whole region as shown in Figure 3. The reason for this is discussed below.

Resistance to flow

Let us consider flow of mass through a thin section. For a steady flow the mass passing through the section will be the same, but the resistance to flow will slow it down. As the material is homogeneous, each section will contribute the same amount of resistance and the velocity will slow down with distance as $v=A/x$, where A is a materials constant, representing the conductivity. This is analogous to the flow of liquids through a capillary tube or an electric current passing through a conductor. As $v=dx/dt$, integration of $\int Adt=\int xdx$ will give $2At=x^2$ or $x=(2At)^{1/2}$ which is the same as $x_0 = 2(Dt)^{1/2}$ for Fickian diffusion. It is thus obvious, that the Fickian rate of diffusion is correct for all homogeneous materials which provide resistance to flow.

Initial stages of diffusion

The above equation is however not realistic at the very beginning of the diffusion process, as the velocities of molecules entering the polymer will have to reach unrealistically high values. Accurate experimental evaluations[9-10)] show that initially the diffusion is slower and that the $t^{1/2}$ relationship is established later. This has been assigned to a delay time needed to establish the diffusion front[10)]. Alternatively it is possible to assume, that the maximum rate of diffusion is limited to B/2 (or $D^{1/2}$) and follows the square root time dependence from this value. This leads to an equation

$x_0=B((kt+1)^{1/2}-1)$ and

$v=B/2(kt+1)^{1/2}$ (1)

where the constant k is a scaling factor. In principle this means, that the Fickian diffusion rate vs. time curve will not start at t=0 but at a time for which the rate is $D^{1/2}$. Another mechanism which can explain the initial slow diffusion could be based on sorption kinetics. The process of surface wetting, formation of double layer and establishment of the diffusion front can be considered as a chemical reaction. The diffusion distance will thus be shortened by a factor $(1\text{-}\exp(-(kt)^{1/2}))$, which gives equations:

$x_0=B((kt)^{1/2}+\exp(-(kt)^{1/2})-1)$ and

$v=(B/2(kt^{1/2}))(1-\exp(-kt^{1/2}))$ (2)

The velocity will again reach a value B/2 (or $D^{1/2}$) as $\lim(t\rightarrow 0)\ (1-\exp(t^{1/2}))/t^{1/2} = 1$. This equation has been used for the explanation of the experimental data for methanol in polymethyl methacrylate and decanoic acid in polystyrene⁹⁾, but its general validity must be verified for other systems.

There are very small differences between equations (1) and (2) (Figure 3a and 3b), and current experiments are not accurate enough to decide unambiguously in favour of one or the other. The experimental errors in establishing accurately the rate of diffusion are due to the inhomogeneity of the polymer as a skin/core effect is always present in moulded samples, and the difficulty in measuring the initial diffusion distances as these are very small.

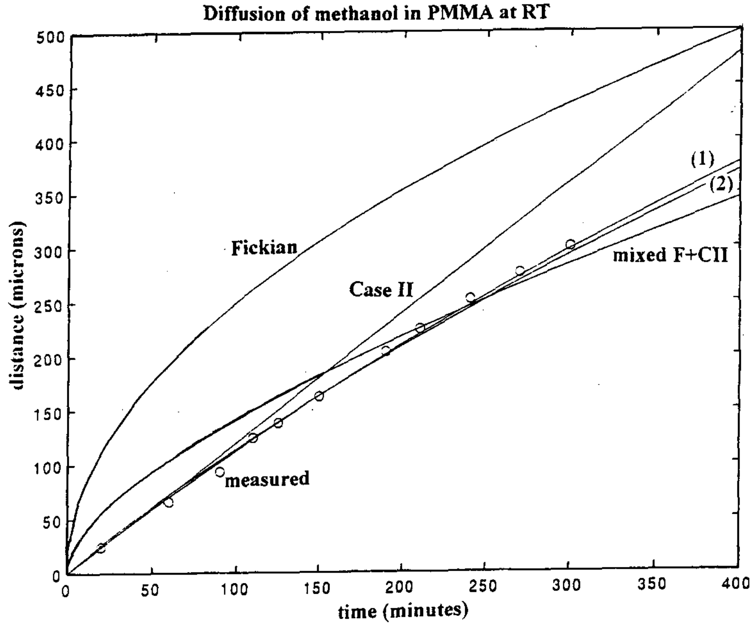

Figure 3a. Experimental data of penetration distance vs.time for methanol diffusing into PMMA at room temperature and the best fit to Fickian, Case II and their combination. The fits for equation (1) and (2) are also shown.

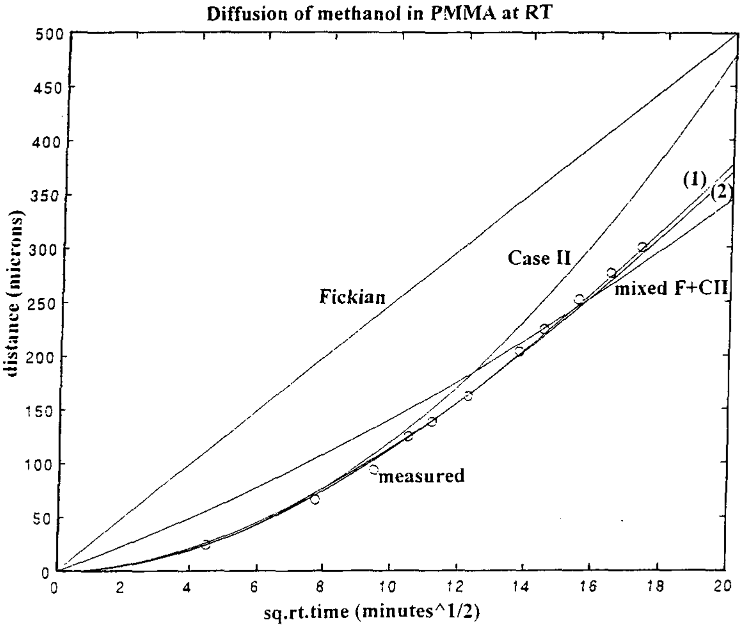

Figure 3b. Experimental data of penetration distance vs. sq.rt.time for methanol diffusing into PMMA at room temperature and the best fit to Fickian, Case II and their combination. The fits for equation (1) and (2) are also shown.

The major consequences of the above analysis are that the slow beginning of diffusion can be wrongly interpreted as linear time dependence, as used for Case II sorption. This is particularly convincing for thin films, which show deviation from this rule only at the last measured points(11). There have been attempts to interpret the deviations by a polynomial $x=at+bt^{1/2}$, but this does not provide a good fit to the data and the initial problem with infinite diffusion rate at the beginning remains. The effect of scaling is illustrated in Figure 4 a,b and c, where identical data for different models are plotted on a different scale. It is shown than any model can be justified by using a suitable scale: for thin films and fast diffusion the small scale will show the linear time dependence. For thick materials and slow diffusion the best fit will be for $t^{1/2}$ dependence. The two new mechanisms proposed here give a very good correlation with experimental data.

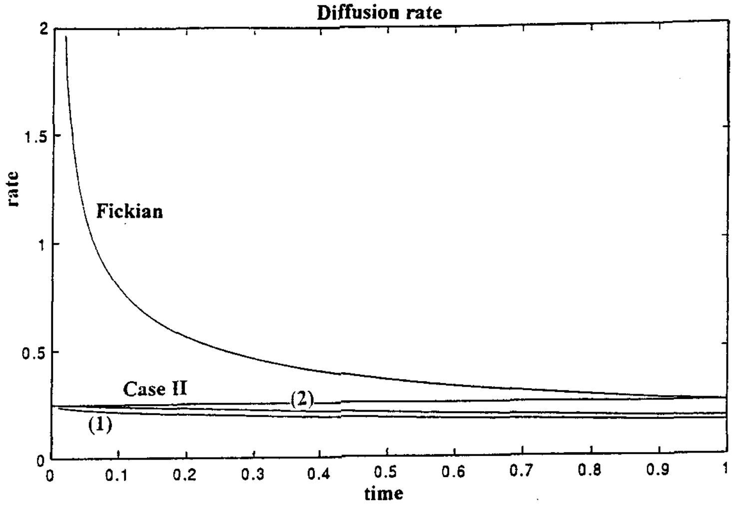

Figure 4a. Rate of diffusion for four different models, plotted on small scale 0-1. Case II fits well to experimental data.

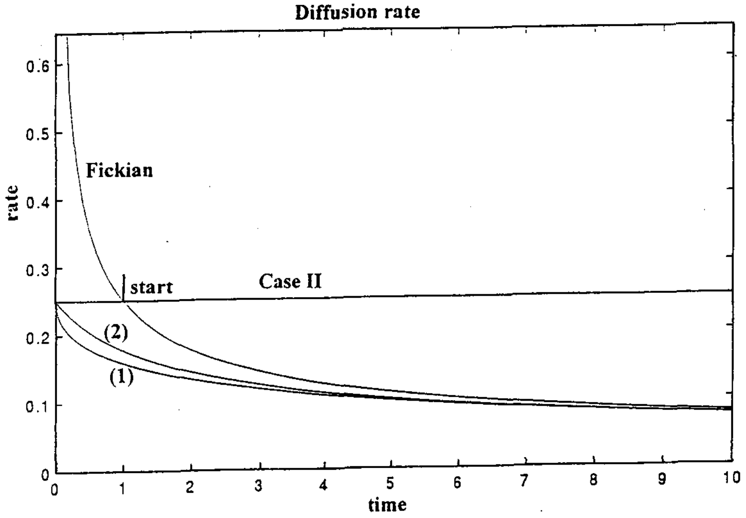

Figure 4b. Rate of diffusion for four different models, plotted on a medium scale 0-10. The differences between models are clearly visible. Equation (1) is identical to Fickian with the start at time =1.

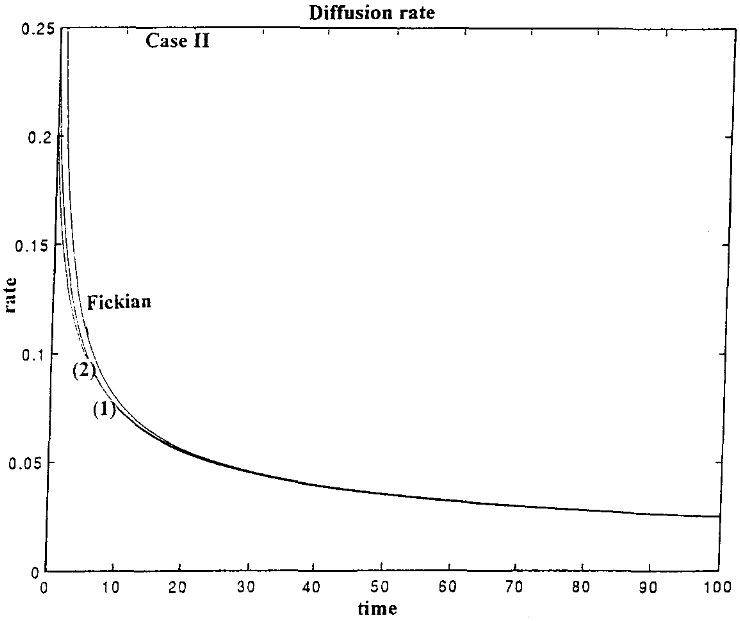

Figure 4c. Rate of diffusion for four different models, plotted on a large scale 0-100. Fickian fits well to experimental data.

Conclusions

1) Fickian diffusion predicts that the diffusion rate is proportional to $1/t^{1/2}$ which is valid for longer time or larger diffusion distances, but requires unrealistically large diffusion rates at the beginning.

2) Case II sorption assumes constant rate of diffusion, i.e. no resistance to flow which has not been observed for larger distances.

3) Mixed Fickian and Case II approach does not provide a good fit to experimental data and the problem with infinite rate at the beginning remains.

4) The experimental data can be accurately interpreted using resistance to flow and limited diffusion rate (equation (1)) or reaction kinetics (equation (2)). It is currently not possible to differentiate between these two mechanisms. The maximum rate of diffusion is $D^{1/2}$ but the meaning of the scaling factor, k has not yet been clarified.

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