Diffusion in Glassy Polymers. Reexamination of Vapor Sorption Data

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ABSTRACT: The sorption data of organic vapor in glassy polymers are reexamined in light of the recently proposed diffusion equation which takes into account both Fickian and case II mechanisms. It is found that the non-Fickian anomalies which include sigmoidal, pseudo-Fickian, and two-stage types can be described adequately with the proposed equation.

In a previous publication,[1] the diffusion process of organic solvent in glassy polymers was discussed in terms of a combination of Fickian and case II mechanisms. The generalized diffusion equation was applied successfully to the analysis of experimental data on diffusion of liquid acetone in a semiinfinite medium of poly(vinyl chloride). It was also suggested[1,2] that literature data on diffusion of organic vapors in glassy polymers could perhaps be reexamined in the same context. In this communication the experimental results of the system methyl acetate–poly(methyl methacrylate) at 30° are analyzed. It is found that the anomalous sorption behavior of the polymer can be represented closely by the generalized equation. In addition, the diffusion coefficient of the system depends on the concentration in a nonexponential manner and falls sharply near zero concentration.

Analysis

The generalized diffusion equation[3,4a] previously derived to describe the combination of Fickian and case II mechanisms is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D\frac{\partial c}{\partial x} - vc\right] \qquad (1)$$

where D is the Fickian diffusion coefficient and v is the velocity of case II diffusion and has been interpreted as a stress coefficient.

In the previous studies of diffusion of liquid solvent into glassy polymers[1,3] the equilibrium solvent concentration C_1 at the polymer surface was very large in each experiment. The sharp advancing front of the solvent in the polymer was accounted for by assuming the diffusion coefficient $D(c)$ to be a step function; $D(c)$ = constant, $C > C_x$ and $D(c) = 0$, $C < C_x$, C_x being the solvent concentration at the moving boundary. Such an assumption is valid if the equilibrium concentration C_1 is much larger than the cut-off concentration C_x so that the swollen part of the polymer is in the rubbery state where D is typically of the order 10^{-7}–10^{-6} cm^2 sec^{-1}. (The diffusion constant of organic molecules in glassy polymers is typically about 10^{-10}–10^{-12} cm^2 sec^{-1}.) In the successive differential sorption experiment, however, the surface concentration of the polymer is increased by a small amount in each successive step. The magnitude of the diffusion constant also undergoes only a modest increase. (In the majority of experiments, the equilibrium concentrations were sufficiently low that the rubbery state was never reached.) Accordingly, it is not necessary to consider the discontinuity in the diffusion coefficient as in the case of liquid diffusion and only an average value of D is needed to describe the Fickian component of the transport phenomenon.

Although the concentration change is small in each sorption step, we still can expect a differential swelling stress to develop in the polymer. The effect of the swelling stress on transport properties is represented by the term v.

In order to apply eq 1 to the results of vapor sorption in thin films, the boundary value problem is solved for a plane sheet with a thickness l and an initial uniform concentration C_0, which is exposed at time $t \geq 0$ to a constant concentration C_1 ($C_1 \neq C_0$) at both surfaces.[4a] Assuming that ($C_1 - C_0$) is small in magnitude and the mean values of D and v can be used in linearizing eq 1, one obtains

$$\frac{C - C_0}{C_1 - C_0} = 1 - \sum_{n=1}^{\infty}(-1)^n 2n\pi \sin\left(\frac{n\pi x}{l}\right)\frac{\left(\cos n\pi - e^{-\frac{vl}{2D}}\right)}{(n\pi)^2 + \left(\frac{lv}{2D}\right)^2} \times \exp\left[-\left(\frac{n^2\pi^2 D}{l^2} + \frac{v^2}{4D}\right)t + \frac{vx}{2D}\right] \qquad (2)^{4b}$$

where x denotes the distance from a surface to an interior point of the film. The net uptake of the solvent by the film per unit surface area is therefore

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty}\frac{4n^2\pi^2\left[1 - (-1)^n \cosh\left(\frac{vl}{2D}\right)\right]}{\left[\left(\frac{vl}{2D}\right)^2 + (n\pi)^2\right]^2} \times \exp\left[-\left(\frac{n^2\pi^2 D}{l^2} + \frac{v^2}{4D}\right)t\right] \qquad (3)$$

where the final equilibrium uptake M_∞ is given by

$$M_\infty = (C_1 - C_0)l$$

Before the above results are compared with experimental data it is perhaps helpful to make a few remarks about the general characteristics of eq 3. Consider an extreme case when the sorption process is entirely due to case II mechanism. Then $D \equiv 0$ and one obtains from eq 1

$$\begin{aligned} \frac{M_t}{M_\infty} &= \frac{2vt}{l} \qquad 0 \leq t \leq \frac{l}{2v} \\ &= 1 \qquad t \geq \frac{l}{2v} \end{aligned} \qquad (4)$$

which describes a parabola with a positive or upward curvature in the transient period when plotted against (time)$^{1/2}$. Since eq 3 represents the combined effects of Fickian and case II mechanisms the same upward trend can be expected to develop in the (time)$^{1/2}$ plot if the case

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(1) T. K. Kwei, T. T. Wang, and H. M. Zupko, *Macromolecules*, **5**, 645 (1972).

(2) T. K. Kwei, *J. Polym. Sci., Part A2*, **10**, 1849 (1972).

(3) H. L. Frisch, T. T. Wang, and T. K. Kwei, *J. Polym. Sci., Part A2*, **7**, 879 (1969).

(4) (a) T. T. Wang, T. K. Kwei, and H. L. Frisch, *J. Polym. Sci., Part A2*, **7**, 2019 (1969). (b) There were typographical errors in eq 29 of 4a. The term $e^{-vx/D}$ should read $e^{vx/2D}$.

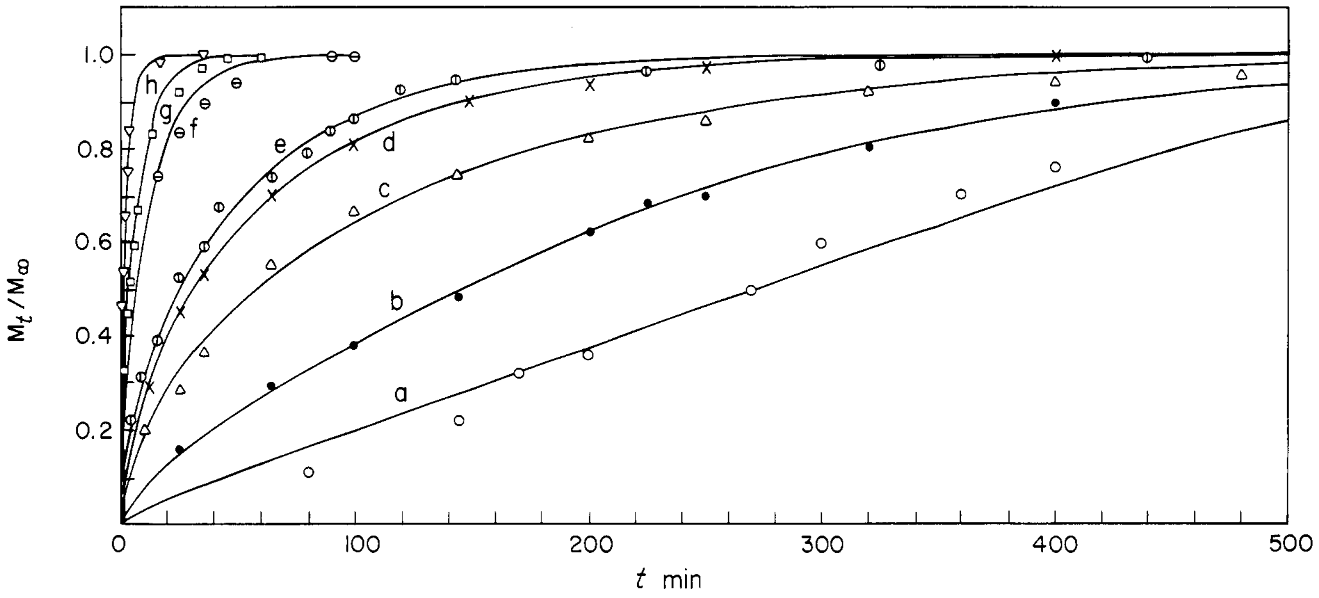

Figure 1. Successive differential sorption data of methyl acetate by poly(methyl methacrylate) at 30°. Solid curves are calculated from eq 3.

Table I
Diffusion Coefficients of Methyl Acetate in PMMA at 30°

Curve	Type of Diffusion	$C_0 \times 10^2$ g/g	Vapor Pressure Increment (mm)	D (cm^2/sec)	v (cm/sec)
a	Sigmoidal	0	0-25	5.0×10^{-13}	2.5×10^{-8}
b	Pseudo-Fickian	1	25-50	5.0×10^{-12}	3.6×10^{-8}
c	Pseudo-Fickian	2	50-66	3.0×10^{-11}	3.6×10^{-8}
d	Pseudo-Fickian	3	66-80	6.5×10^{-11}	3.6×10^{-8}
e	Two stage	6.6	100-110	8.5×10^{-11}	3.6×10^{-8}
f	Two stage	9.2	115-124	3.5×10^{-10}	3.6×10^{-8}
g	Pseudo-Fickian	10.0	124-130	6.0×10^{-10}	3.6×10^{-8}
h	Fickian	12.1	134-140	1.0×10^{-9}	0

II contribution is dominant. This is in qualitative agreement with the general feature of non-Fickian anomalies which are often characterized by an upward curvature and a point of inflection in the sorption curves along the $(\text{time})^{1/2}$ axis.

On the other hand, since the case II sorption curve is linear in t and the Fickian sorption is never convex to the time axis,[5] eq 3 is also likely to describe a sorption curve which is never convex to the time axis. Accordingly, if in the real time plot, the sorption data still exhibit an upward curvature eq 3 will not be able to account for such an anomalous behavior. The above argument suggests that the suitability of eq 3 can perhaps be examined more readily if both the sorption data and the analytical results are plotted against real time.

Comparison with Experiments

Equation 3 will now be employed to describe the sorption data obtained by Kishimoto *et al.*[6] for successive differential sorption of methyl acetate by poly(methyl methacrylate) (PMMA) at 30°. Figure 1 shows the real time plots of analytical results (solid curves) as well as experimental data which include Fickian (curve h), sigmoidal (curve a), pseudo-Fickian (curves b, c, d, g), and two-stage (curves e, f) sorptions. The corresponding values of D and v are summarized in Table I. It is seen that with a proper choice of the parameters D and v the experimental values can be fitted reasonably well with eq 3. The slightly larger scatter in curve a might have resulted from the measurement error incurred at low weight gains.

In curves a and b, which correspond to sorption at lower concentrations or lower vapor pressures, the case II contribution is rather pronounced as indicated by the relatively large v compared with D. At higher concentrations (curves c–h) the sorption behavior is dominated by the Fickian contribution. In curves f and g, for example, omission of the v term in eq 1 results in a change of only a few per cent in the uptake. This is in accord with the assumptions upon which eq 1 is derived since the effect of swelling stress should become progressively less significant with the amount of initial equilibrium concentration.

It should be pointed out that there were four more curves in the original data of Kishimoto *et al.*[6] which were not included in Figure 1. Among these curves, two (C_0 = 0.081 and 0.112 g per g) could be fitted closely with eq 3 but were omitted in the figure for the sake of clarity. The remaining two (C_0 = 0.04 and 0.05 g per g) appeared to have not reached equilibrium at points where the curves were terminated. Nevertheless, when the end points were taken as the equilibrium concentrations in the trial plot, the maximum deviation was less than 15% over the entire range.

In Figure 2 the logarithmic values of D (solid circles) are plotted against the arithmetic average concentration of the solvent in each successive sorption step. At higher concentrations ($C > 0.03$ g/g), log D behaves in a manner

[5] S. Prager in "Mathematics of Diffusion," J. Crank, Ed., Oxford University Press, London, 1956, p 277.

[6] A. Kishimoto, H. Fujita, H. Odani, M. Kurata, and M. Tamura, *J. Phys. Chem.*, **64,** 594 (1960).

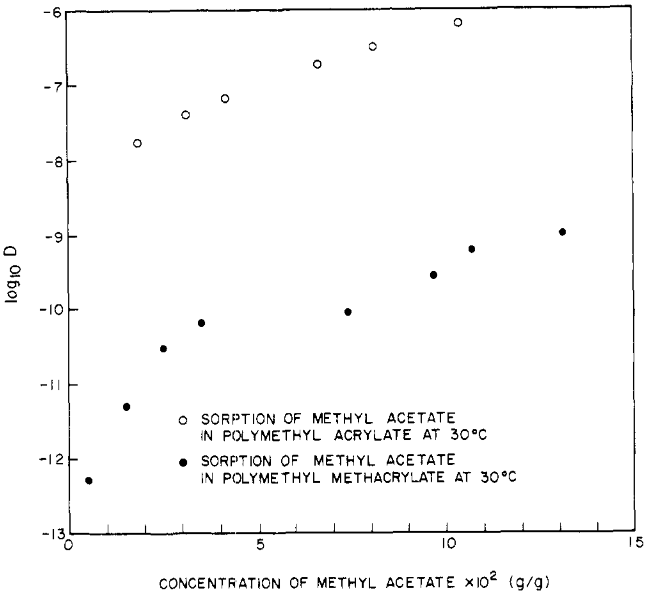

Figure 2. Semilogarithmic plot of the diffusion coefficient against the solvent concentration.

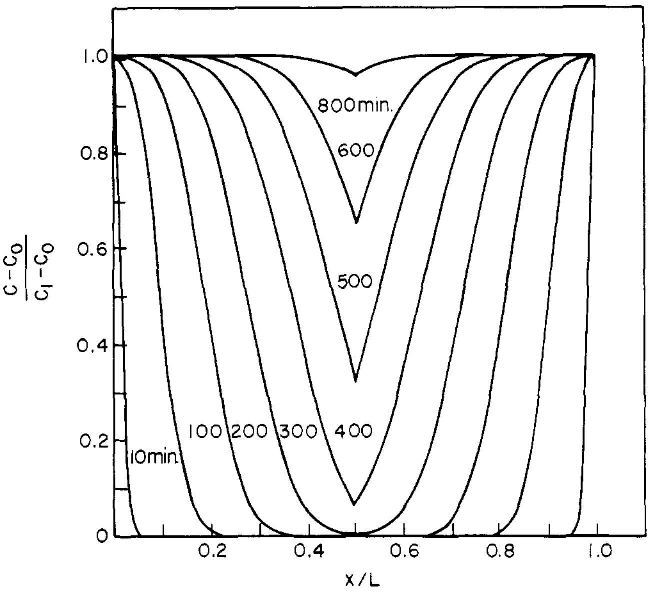

Figure 3. Concentration profiles of solvent across the film thickness at different times.

more or less similar to those found in other amorphous polymer systems tested slightly above the glass temperature (see, for instance, the results of the system methyl acetate-poly(methyl acrylate),[7] hollow circles, in Figure 2). At lower concentrations ($C < 0.03$ g/g), however, the diffusion coefficient drops by as much as two orders of magnitude and reaches a value in the order of about 10^{-13} at zero concentration. This is perhaps not too surprising in view of the recent results on other polymer-diluent systems[7-11] which show an increasingly larger downward curvature as the temperature is lowered toward the glass temperature of the polymer. The results in Figure 2 suggest that such a progressively downward trend is continued to temperatures well below T_g of the polymer.

The sharp changes in the diffusion coefficient also lend support to the assumption made earlier[3,4] that the diffusion coefficient may be approximated as a discontinuous function of concentration when the polymer is in the glassy state at the test temperature.

Before closing it is of interest to examine the distribution of solvent concentration across the film thickness. Figure 3 displays the results calculated from D and v values of curve a, Figure 1 with the aid of eq 2. In the initial period up to about 200 min the concentration profiles resemble those obtained for diffusion in a semiinfinite medium.[1] It may be noted that a certain amount of the surface region is already in a near saturated state even at short times. At larger times, the profiles are seen to form a cusp at the midsection of the film. The discontinuity in the slope across the midsection arises from the stress (second) term in eq 1 as can be verified easily from eq 2. The slope vanishes and becomes continuous across the midpoint when the diffusion process tends to Fickian type.

(7) H. Fujita, A. Kishimoto, and K. Matsumoto, *Trans. Faraday Soc.*, **56**, 424 (1960).

(8) P. Meares, *J. Polym. Sci.*, **27**, 391, 405 (1958).

(9) A. Kishimoto and K. Matsumoto, *J. Phys. Chem.*, **63**, 1529 (1959).

(10) A. Kishimoto and Y. Enda, *J. Polym. Sci., Part A*, **1**, 1799 (1963).

(11) A. Kishimoto, *J. Polym. Sci., Part A*, **2**, 142 (1964).