Diffusion and relaxation in glassy polymer powders: 2. Separation of diffusion and relaxation parameters

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Gravimetric sorption measurements for organic vapours in monodisperse glassy polymer powders have shown widely varied non-Fickian kinetic behaviour. These varied kinetics are interpreted by a single mathematical model involving a linear superposition of one or two phenomenologically independent first order relaxation terms upon the ideal Fickian diffusion equation. Analysis of experimental data for submicron powders through this model yields kinetic and equilibrium parameters describing the individual contributions of the diffusion and relaxation processes. This analysis has been applied to both integral and incremental sorption data for vinyl chloride, acetone, and methanol in poly(vinyl chloride) and for n-hexane in polystyrene. Sorption by initially penetrant-free polymer samples is dominated by a rapid Fickian diffusion process, while incremental sorptions show larger relative contributions from slow relaxation processes. The relaxation processes appear to be related to slow redistribution of available free volume through relatively large scale segmental motions in the relaxing polymer. The diffusion–relaxation model seems to provide a meaningful analysis of several non-Fickian 'anomalies', including a very slow approach to apparent equilibrium, two-stage and sigmoidal sorption curves, and sorption curves involving an initial maximum followed by temporary desorption and subsequent resorption.

INTRODUCTION

When a solid polymer is brought into contact with a penetrating liquid or vapour, the penetrant diffuses into the polymer and the polymer swells. Diffusion involves migration of the small molecules into pre-existing or dynamically formed spaces between polymer chains. Swelling of the polymer involves larger scale segmental motion resulting, ultimately, in an increased distance of separation between polymer molecules.

Both concentration-gradient-controlled diffusion and relaxation-controlled swelling contribute to the rate and extent of penetrant sorption in glassy polymers[1–4]. As the relative contributions of these two processes change, a wide range of behavioural patterns may be encountered. These observed effects vary not only from system to system but also with the temperature and concentration interval in a given penetrant–polymer pair[5]. Hopfenberg and Frisch[6] have suggested that behaviour ranging from ideal Fickian diffusion to limiting Case II (relaxation or swelling-controlled) sorption may be expected for a given penetrant/polymer system if a sufficient range of temperature and penetrant activity is traversed experimentally.

Vrentas, Jarzebski, and Duda[7] suggested that the dimensions of a polymer specimen may affect the relative contribution of diffusion and relaxation since the relaxation process is independent of polymer dimensions but the characteristic times associated with unsteady-state, diffusion-controlled sorption vary directly with the square of the specimen dimension. Even for rather thin films (~20 μm) of glassy polymers, the rates of diffusion and relaxation are often quite similar and, therefore, the observed sorption behaviour reflects a complex superposition of the two processes. Diffusion-controlled sorption into submicron particles may be sufficiently rapid to permit explicit separation of diffusion from dimension-independent relaxation kinetics. In this regard, Enscore *et al.*[8] have demonstrated that under identical conditions of temperature and penetrant activity, n-hexane sorbs into relatively large polystyrene spheres (~ 200 μm diameter) by a relaxation-controlled mechanism whereas Fickian diffusion dominates the n-hexane penetration of submicron polystyrene spheres.

An extensive study of vinyl chloride monomer (VCM) transport in poly(vinyl chloride) (PVC) powder samples has been reported previously[9–12]. The diffusion path in the primary PVC particles comprising the powder samples was much shorter than could practically be attained in film samples. In sorption experiments at very low VCM activities, simple Fickian kinetics were obeyed and equilibrium was achieved in a few minutes, although the diffusion coefficient at 30°C was only 2×10^{-12} cm^2/sec. In sorption experiments covering a larger VCM concentration interval, the initial rapid sorption was followed by a slower further uptake of VCM which was qualitatively attributed to a relaxation-controlled swelling process. These observations were quite similar to the high activity n-hexane sorption experiments in polystyrene microspheres described by Enscore *et al.*[8]. In most cases, the initial (presumably diffusion-controlled) sorption was more rapid than the long term relaxations in these small particle powder samples, permitting explicit separation of the entire sorption process into two seemingly independent mechanisms.

By using these ultra-small particle, powder samples, therefore, an experimental situation was achieved which

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apparently had not been exploited by other researchers. Specifically, the kinetics of diffusion and relaxation could be characterized independently with a single experiment involving the penetration of a glassy polymer by an organic penetrant.

These earlier qualitative observations, regarding the experimental separation of diffusion from polymeric relaxations, prompted the development of the analytical model which is presented in this paper. The suggested model is especially useful for calculation of numerical values of equilibrium and kinetic parameters which describe the respective diffusion and relaxation processes. Most importantly, the model provides a means for calculating a meaningful and useful diffusion coefficient from complex sorption data involving long term relaxations which may overshadow the rapidly achieved Fickian diffusion. Representative experimental data are presented which are profitably interpreted in terms of the diffusion and relaxation parameters calculated from the model. By suitable variation of the model parameters, complex and seemingly unrelated experimental observations are successfully described. The model is also used to analyse the unexpected differences in sorption kinetics between experiments starting with penetrant-free samples (integral sorption) and those involving a finite initial penetrant concentration (incremental sorption).

MODEL FOR EXPLICIT SEPARATION OF DIFFUSION AND RELAXATION PARAMETERS

The sorption process in glassy polymers is considered here as the linear superposition of phenomenologically independent contributions from Fickian diffusion and polymeric relaxations. The total amount of sorption per unit weight of polymeric microspheres at time t may be expressed, therefore, as:

$$M_t = M_{t,F} + M_{t,R} \tag{1}$$

where $M_{t,F}$ and $M_{t,R}$ are the contributions of the Fickian and relaxation processes, respectively, at time t. The purely Fickian process is described by the 'uniform sphere model'[10], expressed as:

$$M_{t,F} = M_{\infty,F}\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2 k_F t)\right] \tag{2}$$

where

$$k_F = 4\pi^2 D/d^2 \tag{3}$$

and $M_{\infty,F}$ is the equilibrium amount of sorption in the unrelaxed polymer, D is the diffusion coefficient, and d is the particle diameter. The relaxation process is assumed to be first order in the concentration difference which drives the relaxation. The differential equation for the relaxation process is therefore:

$$\frac{\mathrm{d}M_{t,R}}{\mathrm{d}t} = k(M_{\infty,R} - M_{t,R}) \tag{4}$$

where k is the relaxation-rate constant and $M_{\infty,R}$ is the ultimate amount of sorption due to relaxation. Integration of equation (4) leads to:

$$M_{t,R} = M_{\infty,R}[1 - \exp(-kt)] \tag{5}$$

Since viscoelastic processes in polymers are often described phenomenologically by a distribution of relaxation times, a more useful and general expression for the relaxation-controlled swelling, consistent with the implied mechanism and the resulting form of equation (5) is:

$$M_{t,R} = \sum_i M_{\infty,i}[1 - \exp(-k_i t)] \tag{6}$$

where each k_i is the respective relaxation rate constant and each $M_{\infty,i}$ represents the equilibrium sorption of the ith relaxation process.

Substitution of equations (6) and (2) into equation (1) results in:

$$M_t = M_{\infty,F}\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2 k_F t)\right] + \sum_i M_{\infty,i}[1 - \exp(-k_i t)] \tag{7}$$

Equation (7) is, therefore, an analytical representation of a model which explicitly separates contributions related to diffusion from those related to first order relaxations. The parameters associated with diffusion are $M_{\infty,F}$ and $k_F = 4\pi^2 D/d^2$ and the parameters describing the relaxations are the respective $M_{\infty,i}$s and k_is.

Several authors[1,13,14] have previously introduced a time dependent relaxation of the surface concentration to model the complex behaviour observed during sorption of organic penetrants in glassy polymers. The surface concentration was assumed to relax according to a first-order expression of the form $C = C_0\,[1 - \exp(-kt)]$. Fickian diffusion driven by a concentration gradient was considered, however, as the sole mechanism producing sorption. The drifting surface concentration, in this view, accounted for the time dependent sorption anomalies.

The physical situation implied by the model embodied in equation (7) is fundamentally different from the previously suggested models although the relaxation terms are similar in form. The model presented here assumes that the Fickian contribution is driven by a gradient which is related to the invariant equilibrium concentration $M_{\infty,F}$. The relaxation terms in equation (7) are independent of particle size and are related to the dissipation of swelling stresses induced by entry of the penetrant. This dissipation, or stress relaxation, is initiated by the plasticizing penetration but is considered here to be otherwise independent of the superimposed diffusive transport. Since the relaxation processes are size independent and the parameter k_F varies with $1/d^2$, the rate-controlling sorption mechanism will vary with particle size. If d is sufficiently small, such that $k_F \gg k_i$, then a rapid Fickian first stage will precede a slower, discernably separable, second stage of relaxation-controlled sorption. For a larger d such that $k_F \cong k_i$ the two stages would not be clearly separated.

It is helpful to consider a series of curves representing equation (7) with arbitrarily varied diffusion and relaxation parameters to demonstrate graphically the effects of varying

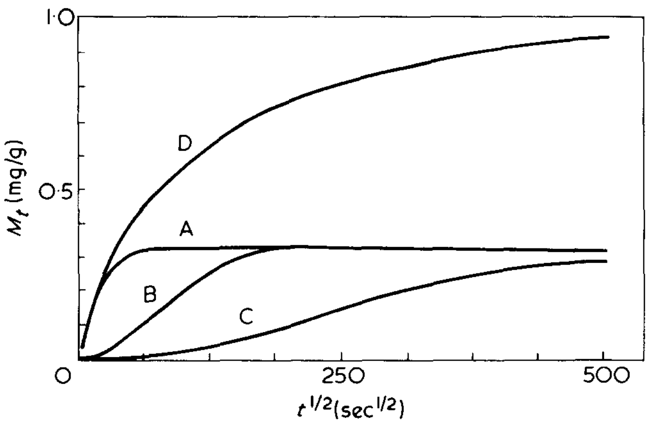

Figure 1 Sorption curves, M_t vs. $t^{1/2}$, calculated from equation (7) with $M_{\infty F} = M_{\infty 1} = M_{\infty 2} = 0.33$ mg/g. A, $k_F = 10^{-3}$ sec^{-1}, $k_1 = k_2 = 0$; B, $k_F = 0$, $k_1 = 10^{-4}$ sec^{-1}, $k_2 = 0$; C, $k_F = k_1 = 0$, $k_2 = 10^{-5}$ sec^{-1}; D, $k_F = 10^{-3}$, $k_1 = 10^{-4}$, $k_2 = 10^{-5}$ sec^{-1}

the relative contributions of diffusion and relaxation upon the overall sorption kinetics. In these calculated plots, as well as in the plots presenting experimental data, the weight gain of the polymer sample is plotted against $t^{1/2}$, which is the conventional time coordinate suggested by simple Fickian sorption kinetics. In the calculated plots of *Figure 1*, the individual contributions of a Fickian term and two relaxation terms, with $k_F > k_1 > k_2$ and $M_{\infty,F} = M_{\infty,1} = M_{\infty,2}$ are compared with the summation of the three terms. The amount sorbed by Fickian diffusion plotted against $t^{1/2}$ yields a curve which is continually concave toward the $t^{1/2}$ axis. In contrast, plots of the relaxation-controlled contributions to sorption (e.g. $M_{t,1}$ or $M_{t,2}$), exhibit an inflection point. Nevertheless, for these arbitrarily selected parameters, the summation curve shows no region of upward curvature. Thus, while upward curvature over a portion of an M_t *versus* $t^{1/2}$ curve indicates the presence of a relaxation-contribution to the overall sorption, the absence of upward curvature does not, in general, preclude the contribution of a relaxation process.

The analytical representation of the pure relaxation contribution, represented by equation (6), is intriguingly similar to the analytical result presented earlier for limiting Case II transport in spheres. Enscore *et al.*[8] present the relationship between fractional sorption and time as:

$$\frac{M_t}{M_\infty} = 1 - \left(1 - \frac{k_0 t}{C_0 a}\right)^3 \tag{9}$$

where k_0 is the Case II relaxation constant, C_0 is the equilibrium sorption, and a is the sphere radius. The graphical representation of equation (6), e.g. curves B and C of *Figure 1*, is qualitatively similar to the graphical representation[8] of equation (9). Expansion of equation (9) into an unfactored series yields:

$$\frac{M_t}{M_\infty} = 3\frac{k_0 t}{C_0 a} - 3\left(\frac{k_0 t}{C_0 a}\right)^2 + \left(\frac{k_0 t}{C_0 a}\right)^3 \tag{10}$$

Expansion of the exp(−*kt*) term in equation (6), for small values of k_t results in an infinite series approximation to equation (6) of the form:

$$\frac{M_{t,R}}{M_{\infty,R}} = kt - \frac{(kt)^2}{2!} + \frac{(kt)^3}{3!} + \ldots \qquad (11-$$

The similarity in form between the first three terms of equation (11) and equation (10) suggests a possible relationship between the gradient-free relaxations described by equation (6) and the relaxations associated with the step profile of concentration in Case II transport.

Overall M_t *versus* $t^{1/2}$ curves calculated from equation (7) using a Fickian term and a single relaxation term with $M_{\infty,F} = M_{\infty,1}$ and $k_F > k_1$ are plotted in *Figure 2*. The contribution from the relaxation term is quite apparent when $k_F/k_1 \gg 1$, but becomes less pronounced as the ratio decreases. When k_F approaches k_1, the curves appear nearly Fickian. It may be difficult, therefore, to detect experimentally the existence of a relaxation process if the relaxation rate is comparable to the rate of the Fickian process. The use of smaller diameter particles may, however, increase k_F sufficiently to permit clear separation of the Fickian and relaxation terms.

Additional examples of curves calculated from equation (7) using two relaxation terms are presented in *Figures 3* and *4*. The model predicts a wide variety of kinetic responses as the relaxation rate constants (*Figure 3*) or the equilibrium contributions, $M_{\infty,i}$ (*Figure 4*) are varied.

In practice, two relaxation terms have been found adequate to fit even the most complex experimental sorption data. The value of the model, however, is not limited to the

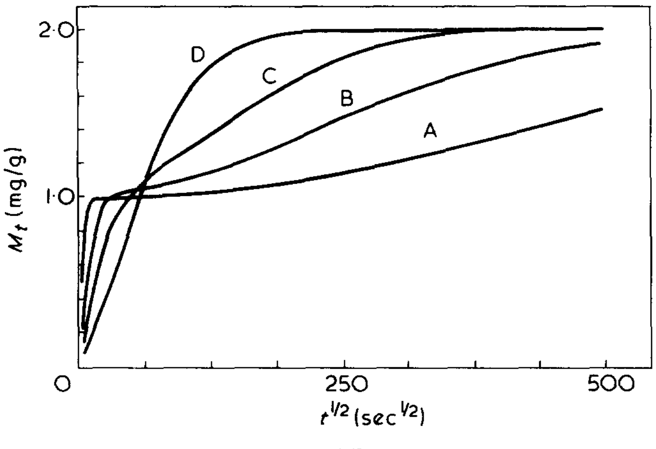

Figure 2 Sorption curves, M_t vs. $t^{1/2}$, calculated from equation (7) with $M_{\infty F} = M_{\infty 1} = 1.0$ mg/g, $k_2 = 0$. A, $k_F = 3 \times 10^{-2}$, $k_1 = 3 \times 10^{-6}$ sec^{-1}; B, $k_F = 5 \times 10^{-3}$, $k_1 = 1 \times 10^{-5}$ sec^{-1}; C, $k_F = 1 \times 10^{-3}$, $k_1 = 3 \times 10^{-5}$ sec^{-1}; D, $k_F = 3 \times 10^{-4}$ $k_1 = 1 \times 10^{-4}$ sec^{-1}

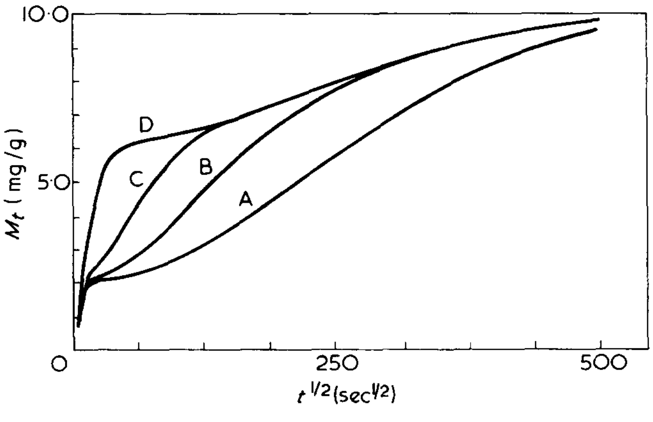

Figure 3 Sorption curves, M_t vs. $t^{1/2}$, calculated from equation (7) with $M_{\infty F} = 2.0$, $M_{\infty 1} = M_{\infty 2} = 4.0$ mg/g, $k_F = 10^{-2}$, $k_2 = 10^{-5}$ sec^{-1}. A, $k_1 = 10^{-5}$ sec^{-1}; B, $k_1 = 5 \times 10^{-5}$ sec^{-1}; C, $k_1 = 2 \times 10^{-4}$ sec^{-1}; D, $k_1 = 2 \times 10^{-3}$ sec^{-1}

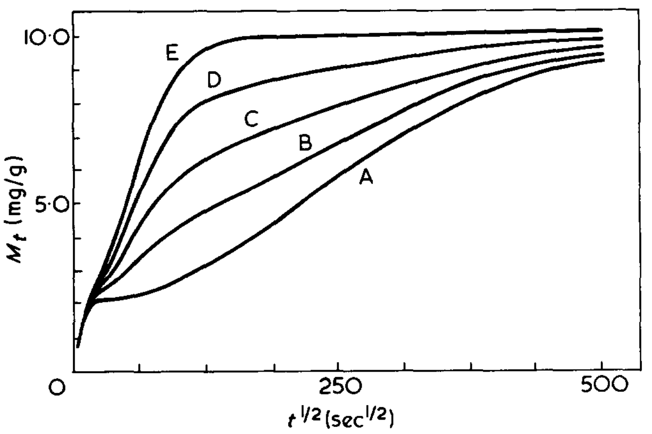

Figure 4 Sorption curves, M_t vs. $t^{1/2}$, calculated from equation (7) with $M_{\infty F}$ = 2.0 mg/g, $k_F = 10^{-2}$, $k_1 = 2 \times 10^{-4}$, $k_2 = 10^{-5}$ sec^{-1}. A, $M_{\infty 1}$ = 0, $M_{\infty 2}$ = 8.0 mg/g; B, $M_{\infty 1}$ = 2.0, $M_{\infty 2}$ = 6.0 mg/g; C, $M_{\infty 1} = M_{\infty 2}$ = 4.0 mg/g; D, $M_{\infty 1}$ = 6.0, $M_{\infty 2}$ = 2.0 mg/g; E, $M_{\infty 1}$ = 8.0 mg/g, $M_{\infty 2}$ = 0

successful fitting of experimental data with the six parameters, $M_{\infty,F}$, $M_{\infty,1}$, $M_{\infty,2}$, k_F, k_1 and k_2. More importantly, the model provides an intuitively satisfying separation of diffusional and relaxation-controlled effects which have been observed experimentally for sorption in PVC[11,12] and polystyrene[8,15] microspheres. Data analysis through this model provides reasonable estimates of diffusion coefficients and permits quantitative, albeit phenomenological, characterization of concurrent relaxation processes. In order to demonstrate conclusively that the model has fundamental as well as phenomenological significance, it will be necessary to test experimentally the particle size dependence of k_F and independence of the k_is, and to demonstrate activation energies which are consistent with diffusion and relaxation processes, respectively.

EXPERIMENTAL

Materials

The PVC sample was an experimental powder of uniform particle size prepared by emulsion polymerization at 50°C. The powder sample was maintained at room temperature after polymerization. The particle diameter determined by electron microscopy was 0.44 μm, which was consistent with the specific surface area of 9.8 m^2/g determined by nitrogen adsorption.

The polystyrene sample was also prepared by emulsion polymerization. Its particle diameter was 0.534 μm as determined by light scattering using the higher order Tyndall spectrum and 0.533 μm by transmission electron microscopy.

Reagent grade n-hexane, methanol and acetone were used after repeated evacuation to remove dissolved gases. Research grade vinyl chloride monomer was used without further purification.

Apparatus and procedure

PVC experiments. The time dependent weight change of a PVC powder sample upon exposure to a predetermined pressure of penetrant vapour was determined with a Cahn Electrobalance. A detailed description of the experimental procedure has previously been published[10].

Polystyrene experiments. The vapour sorption experiments in polystyrene were performed using a McBain quartz spring balance system rather than a recording electrobalance. In all other respects, however, the experimental procedures in the polystyrene experiments were identical to procedures used with PVC. A more detailed description of this experimental technique has been presented by Jacques and Hopfenberg[16].

RESULTS AND DISCUSSION

Experimental results are presented for VCM, acetone, and methanol sorption in 0.44 μm diameter, emulsion-polymerized PVC and also for n-hexane sorption in 0.534 μm diameter, emulsion-polymerized polystyrene. Experiments in which the penetrant pressure and, in turn, penetrant concentration in the polymer are raised from zero to a higher value are termed integral sorptions. Sorption experiments starting with the polymer and vapour in apparent equilibrium at a finite, non-zero pressure, and proceeding to a higher pressure, are termed incremental sorptions. The terms 'integral' and 'incremental' as used here thus refer only to the initial conditions of a sorption experiment, rather than to the magnitude of the pressure interval or final pressure.

In all cases, the parameters of equation (7) have been obtained from the experimental data by a trial and error computer-assisted fitting routine. Initial trial values of k_F, k_1, and k_2 are intuitively selected by inspection of a plot of experimental M_t data *versus* $t^{1/2}$. Since all of the experiments reported here involved submicron particles and exhibited very rapid initial rates of sorption, the trial values of k_F were estimated from the initial portion of the M_t vs. $t^{1/2}$ curves, and the longer time data were used to estimate k_1 and k_2. The computer program calculates values of $M_{\infty,F}$, $M_{\infty,1}$, and $M_{\infty,2}$ which minimize the summed-squares deviations between the data and the corresponding values calculated from equation (7) using the trial values of the ks. The quality of the fit is evaluated subjectively from plots of calculated and experimental data. New values of k_F, k_1, and k_2 are then judiciously introduced into the program until a satisfactory fit between model and experiment is achieved.

VCM sorption in PVC

Data for integral sorption of VCM in PVC at 30°C to final relative pressures, P_{rel}, of 0.02 and 0.10 are presented in *Figures 5* and *6*, respectively. The constants of equation

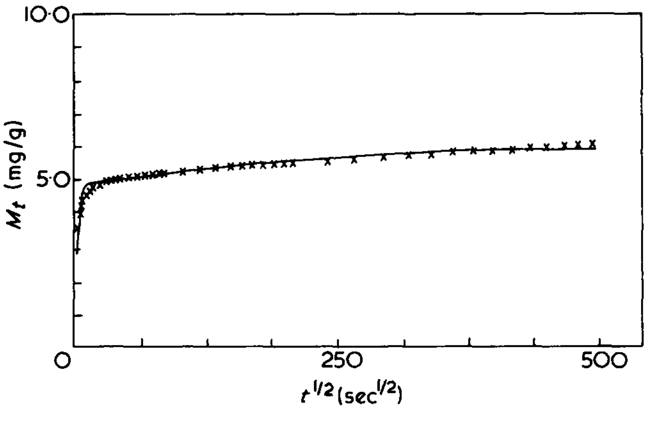

Figure 5 M_t vs. $t^{1/2}$ for sorption of VCM by PVC (0.44 μm powder) at 30°C, P_{rel} = 0 → 0.020. x, Experimental; ——, equation (7) with $M_{\infty F}$ 4.783, $M_{\infty 1}$ = 0.264, $M_{\infty 2}$ = 0.700 mg/g; $k_F = 4.5 \times 10^{-2}$, $k_1 = 5 \times 10^{-4}$, $k_2 = 2.2 \times 10^{-5}$ sec^{-1}

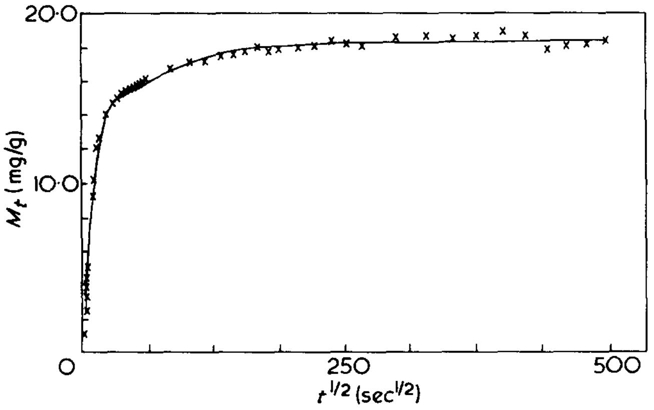

Figure 6 M_t vs. $t^{1/2}$ for sorption of VCM by PVC at 30°C, P_{rel} = 0 → 0.100. x, Experimental; ——, equation (7) with $M_{\infty F}$ = 14.740, $M_{\infty 1}$ = 3.699, $M_{\infty 2} \cong 0$ mg/g; $k_F = 3.8 \times 10^{-3}$, $k_1 = 1 \times 10^{-4}$, $k_2 = 5 \times 10^{-5}$ sec^{-1}

(7) fitted to the data, and the corresponding calculated curves, are also given in the Figures. The analyses suggest that Fickian diffusion accounts for 80 to 90% of the total VCM sorbed in these experiments. The half-sorption time of the Fickian process is less than 10 sec, and the diffusivity calculated from k_F is approximately 2×10^{-12} cm^2/sec, in good agreement with D obtained in experiments at lower P_{rel} where simple Fickian behaviour was observed[10]. The half-times associated with the relatively minor relaxation-controlled contributions here are of the order of hours.

The initial rapid stage of sorption may be related to the Fickian diffusion of penetrant into pre-existing and available vacancies or sites in the glassy polymer. The amount of penetrant sorbed by this process varies with the previous thermal and swelling history of the polymer sample[9,10,15], i.e. with factors which are expected to alter the frozen-in free volume of the sample. The relaxation processes, which occur over a longer time-scale than diffusion in submicron particles, may be related to a structural reordering or redistribution of free-volume elements to provide additional sites of suitable size and accessability to accommodate more penetrant molecules.

The incremental sorption curves determined at 30°C over the P_{rel} intervals 0.02–0.05 and 0.05–0.10 are presented in *Figures 7* and *8*, respectively. The curves of *Figures 5*, *7* and *8* therefore represent a three-step approach to the same final pressure as the integral sorption run of *Figure 6*. The relative contribution of the rapid Fickian process is significantly less, and that of the slower relaxation processes is correspondingly greater, in the incremental runs (*Figures 7* and *8*) than in the integral runs (*Figures 5* and *6*). In the incremental sorption from P_{rel} = 0.05 to 0.10, for example, the Fickian term accounts for only 40% of the total sorption, while in the integral sorption to P_{rel} = 0.10 the Fickian contribution was over 80% of the total sorption achieved in 70 h. The total uptake of penetrant in an integral sorption and in a series of incremental sorptions ending at the same relative pressure are quite similar despite the substantial difference in the relative contributions of diffusion and relaxation in the two types of experiment.

These and other comparisons of integral and incremental sorption experiments have consistently shown that the rapid Fickian process dominates the overall sorption by initially penetrant-free polymer samples, while the slower relaxations are relatively much more important for sorption in samples initially equilibrated with finite amounts of penetrant. Presumably, more complex behaviour is observed, in general, for incremental sorptions than for integral sorptions since incremental sorptions, by definition, proceed with a polymeric specimen in which the most available pre-existing sorption sites have been pre-saturated. The relative contribution of long-term relaxations is, therefore, significantly larger in the incremental experiments since the pre-existing sites required for rapid Fickian diffusion into the glass have been previously filled and the rate-determining step of absorption is redistribution of the available free volume into size elements sufficient to accommodate additional penetrant. These redistribution processes are inherently much slower than simple diffusion into pre-existing cavities.

Acetone sorption in PVC

The experimental data, fitted model parameters, and calculated curve for the integral sorption of acetone in the 0.44 μm PVC powder at 30°C to P_{rel} = 0.19 are shown in *Figure 9*. The major portion of this sorption occurred in the first few minutes; the slower relaxation process, with a half-time of about 10 h, accounts for less than 20% of the total sorption. Incremental sorption data for acetone in PVC over the P_{rel} interval 0.05–0.10, are presented in *Figure 10*. As in the VCM/PVC system, long-term relaxations play a

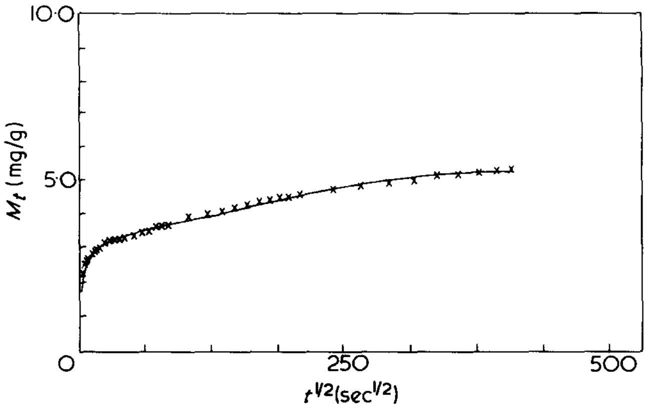

Figure 7 M_t vs. $t^{1/2}$ for sorption of VCM by PVC at 30°C, P_{rel} = 0.020 → 0.050. X, Experimental; ——, equation (7) with $M_{\infty F}$ = 2.974, $M_{\infty 1}$ = 0.405, $M_{\infty 2}$ = 1.894 mg/g, $k_F = 4 \times 10^{-2}$, $k_1 = 1 \times 10^{-3}$, $k_2 = 2.2 \times 10^{-5}$ sec^{-1}

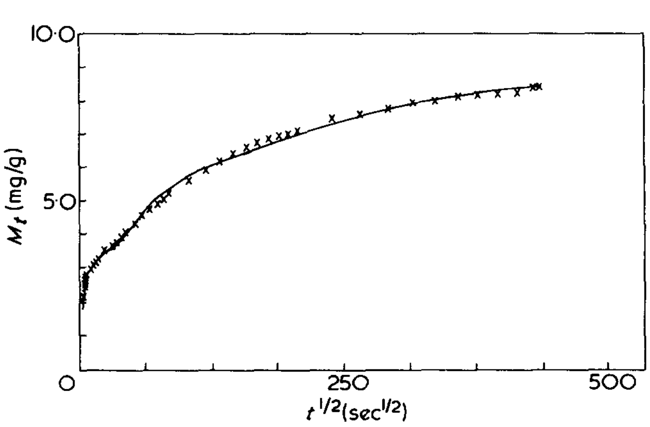

Figure 8 M_t vs. $t^{1/2}$ for sorption of VCM by PVC at 30°C, P_{rel} = 0.050 → 0.100. X, Experimental; ——, equation (7) with $M_{\infty F}$ = 3.094, $M_{\infty 1}$ = 2.475, $M_{\infty 2}$ = 3.025 mg/g; $k_F = 4 \times 10^{-2}$, $k_1 = 2.2 \times 10^{-4}$, $k_2 = 1.4 \times 10^{-5}$ sec^{-1}

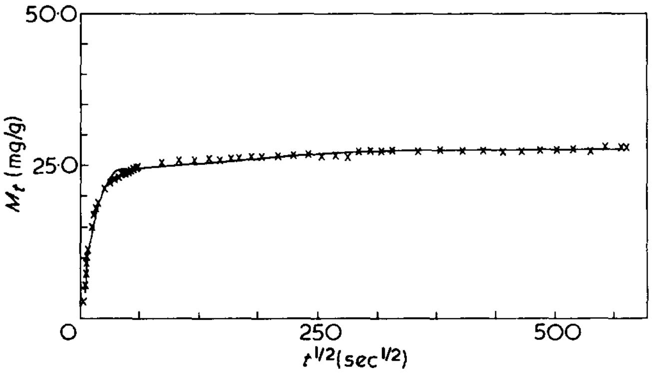

Figure 9 M_t vs. $t^{1/2}$ for sorption of acetone by PVC at 30°C, P_{rel} = 0 → 0.194. X, Experimental; ——, equation (7) with $M_{\infty F} = 9.767$, $M_{\infty 1} = 14.520$, $M_{\infty 2} = 3.434$ mg/g; $k_F = 3 \times 10^{-2}$, $k_1 = 2.5 \times 10^{-3}$, $k_2 = 2.2 \times 10^{-5}$ sec^{-1}

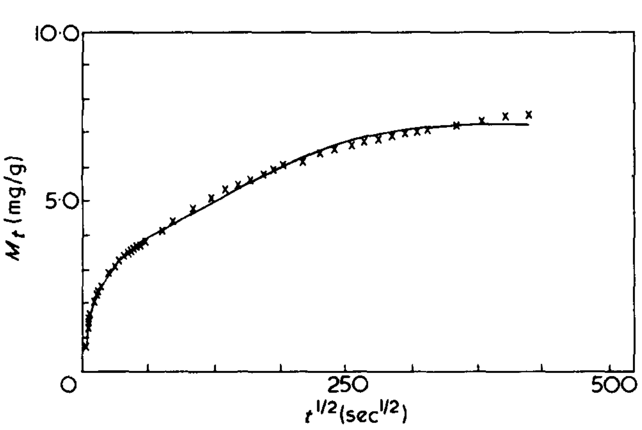

Figure 10 M_t vs. $t^{1/2}$ for sorption of acetone by PVC at 30°C, P_{rel} = 0.053 → 0.103. X, Experimental; ——, equation (7) with $M_{\infty F}$ = 1.899, $M_{\infty 1} = 1.671$, $M_{\infty 2} = 3.762$ mg/g, $k_F = 2.1 \times 10^{-2}$, k_1 = 1×10^{-3}, $k_2 = 3 \times 10^{-5}$ sec^{-1}

relatively greater role in the incremental experiments, in contrast to the diffusion-dominated integral sorptions. Again, the apparent equilibrium penetrant content at the same final P_{rel} is very similar for both integral and incremental experiments. The single sorption isotherm obtained from both types of experiments at varied P_{rel} is shown in *Figure 11*; the concave-downward curvature suggests that dual-mode sorption[17] occurs in the acetone–PVC system. Although the solubilities of acetone and VCM in PVC are quite comparable, the diffusivity of acetone calculated from k_F is 5×10^{-13} cm^2/sec, approximately one-fourth that of VCM. The lower diffusivity probably reflects the larger molecular dimensions of acetone compared to VCM.

Methanol sorption in PVC

Data, fitted model parameters, and calculated curves describing integral methanol sorption experiments in PVC at 30°C to final relative pressures of 0.015, 0.049, and 0.20 are shown in *Figures 12–14*, respectively. The apparent equilibrium uptake is roughly an order of magnitude lower for methanol in PVC than for VCM or acetone at similar relative pressures. The diffusivity of methanol in PVC at 30°C, approximately 4×10^{-12} cm^2/sec, as estimated from k_F, is about twice that of VCM, in qualitative accord with the relative molecular size of these penetrants.

Relaxation-controlled contributions are clearly more evident in the integral sorption experiments with methanol than in comparable experiments with VCM or acetone, and become increasingly important as the final P_{rel} of methanol is reduced. The lower penetrant uptake with methanol, compared to VCM or acetone, apparently retards the free-volume redistribution controlling the relaxation process. As the relative pressure of methanol is reduced, this effect is magnified, and the long-term relaxations increasingly dominate the overall sorption kintics.

Experimental data for the incremental sorption of methanol over the P_{rel} interval 0.055–0.096 are presented in *Figure 15*. Without exception, methanol/PVC incremental sorption runs exhibited similar complex behaviour involving a rapid increase to a maximum, followed by a decrease to a minimum and finally by a long, slow increase. These consistent qualitative features were unique to the methanol incremental sorption experiments. The diffusion/relaxation model is especially useful for describing these complex kinetics, since they can be modelled quite accurately by allowing the coefficient of one relaxation term, e.g. $M_{\infty,1}$, to assume a negative value. This negative coefficient implies a desorption of some of the previously sorbed penetrant, perhaps involving a collapse or deswelling of the glassy structure. Methanol is a non-solvent for PVC, but the other penetrants studied here, in contrast, are swelling agents for the poly-

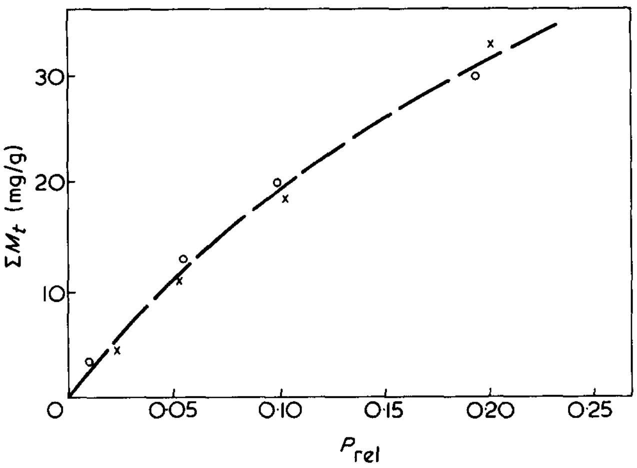

Figure 11 Apparent equilibrium sorption isotherm for acetone in PVC at 30°C. O, Integral sorption; X, incremental sorption

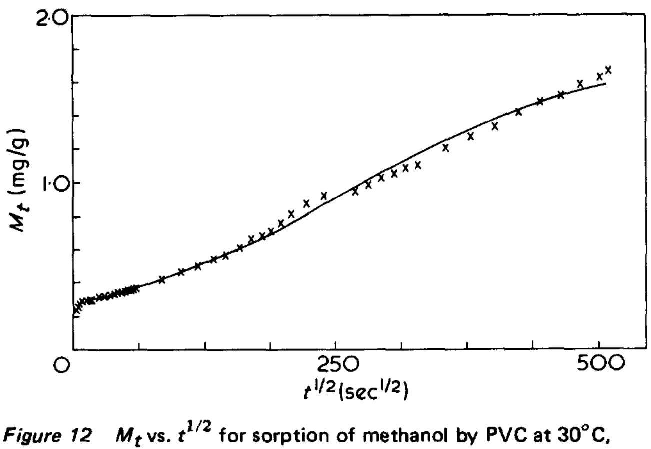

Figure 12 M_t vs. $t^{1/2}$ for sorption of methanol by PVC at 30°C, P_{rel} = 0 → 0.015. X, Experimental; ——, equation (7) with $M_{\infty F}$ = 0.292, $M_{\infty 1} = 0.054$, $M_{\infty 2} = 1.416$ mg/g; $k_F = 8 \times 10^{-2}$, $k_1 = 3.4 \times 10^{-4}$, $k_2 = 8 \times 10^{-6}$ sec^{-1}

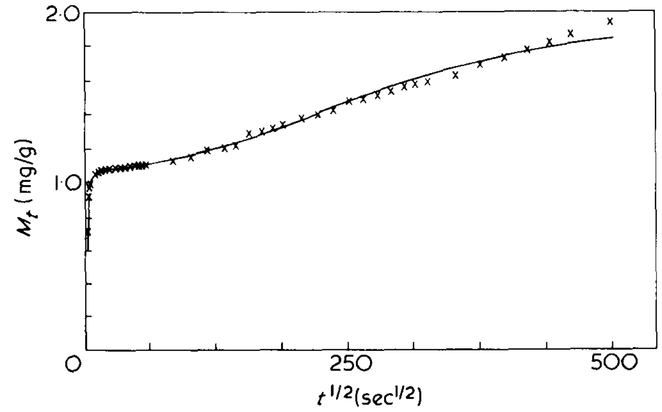

Figure 13 M_t vs. $t^{1/2}$ for sorption of methanol by PVC at 30°C, $P_{rel} = 0 \rightarrow 0.049$. X, Experimental; ——, equation (7) with $M_{\infty F} = 1.076$, $M_{\infty 1} = 0.822$ mg/g; $k_F = 4 \times 10^{-2}$, $k_1 = 1 \times 10^{-5}$ sec^{-1}

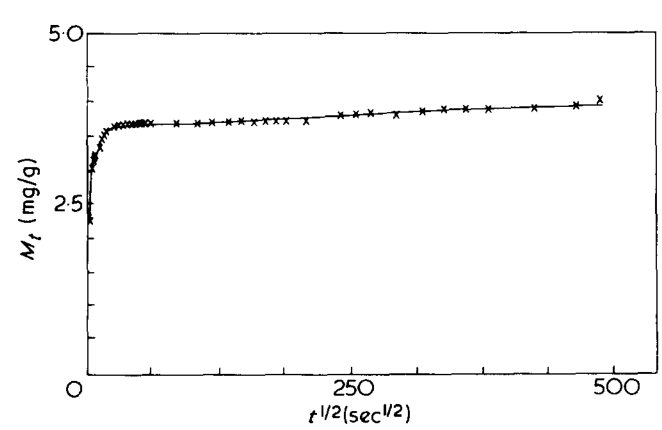

Figure 14 M_t vs. $t^{1/2}$ for sorption of methanol by PVC at 30°C $P_{rel} = 0 \rightarrow 0.203$. X, Experimental; ——, equation (7) with $M_{\infty F} = 3.188$, $M_{\infty,1} = 0.449$, $M_{\infty 2} = 0.343$ mg/g; $k_F = 7.5 \times 10^{-2}$, $k_1 = 4.8 \times 10^{-3}$, $k_2 = 1.3 \times 10^{-5}$ sec^{-1}

mer. No evidence of deswelling during sorption experiments was observed, therefore, for the more highly sorbing penetrants. The increased amount of sorption in the methanol integral sorption experiments presumably 'masks' the negative relaxations (consolidations, desorption) which are readily apparent in the incremental sorptions.

n-Hexane sorption in polystyrene

Examples of integral and incremental sorption data for n-hexane penetration in 0.534 μm polystyrene microspheres are presented in *Figures 16* and *17*, respectively. The diffusion-relaxation model, with constants determined by the fitting program, is again capable of close agreement with the rather widely varied experimental M_t vs. $t^{1/2}$ curves. The distinctly two-stage sorption curve of the incremental experiment presented in *Figure 17*, for example, is well represented by a single relaxation term superposed upon a Fickian diffusion process. As in the experiments with PVC, integral sorptions of n-hexane in polystyrene are dominated by the rapid Fickian diffusion process, while incremental experiments exhibit relatively larger contributions of slower, relaxation-controlled sorption. The similarity in the form of the sorption kinetics for polystyrene and PVC suggests that the controlling relaxations are assocated with glassy state processes *per se* rather than with any special structural features of the crystallizable PVC.

CONCLUSIONS

The absorption of a variety of vapours by glassy PVC or polystyrene microspheres in characterized by a rapid initial uptake of vapour followed by a relatively slow approach to an apparent equilibrium. The relatively rapid first stage of sorption agrees quite satisfactorily with a simple Fickian diffusion model; diffusion coefficients calculated from the initial rate of sorption are consistent with estimates and experimentally determined values for diffusion coefficients in related macroscopic systems.

The relatively slow, long term sorption appears to be related to molecular reordering described phenomenologically by one or two functionally independent first-order relaxation terms. The relative contribution of these relaxations to the overall observed sorption appears to be significantly greater for incremental rather than integral sorption experiments. The extent of sorption is affected by the thermodynamic properties of the polymer and penetrant in question, by the magnitude of the relative pressure interval, and by the previous history of the polymer sample.

The initial rapid Fickian sorption apparently involves the diffusion of penetrant molecules into available, pre-existing free-volume elements ('holes', 'sites'). Polymeric relaxations, involving larger scale (and, therefore, slower) segmental motion, provide a redistribution of the free-volume elements

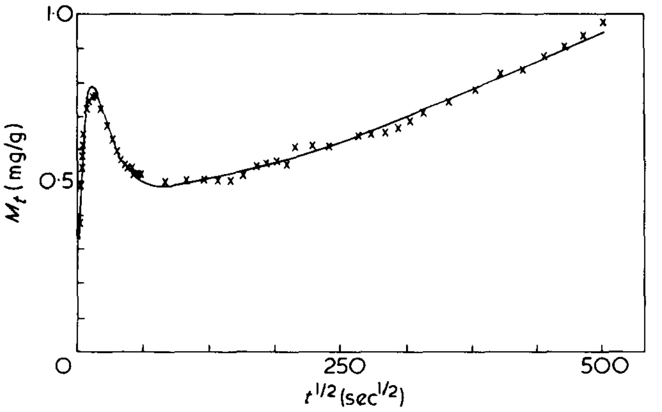

Figure 15 M_t vs. $t^{1/2}$ for sorption of methanol by PVC at 30°C, $P_{rel} = 0.055 \rightarrow 0.096$. X, Experimental; ——, equation (7) with $M_{\infty F} = 0.872$, $M_{\infty 1} = -0.404$, $M_{\infty 2} = 0.892$ mg/g; $k_F = 1.5 \times 10^{-2}$, $k_1 = 8 \times 10^{-4}$, $k_2 = 3 \times 10^{-6}$ sec^{-1}

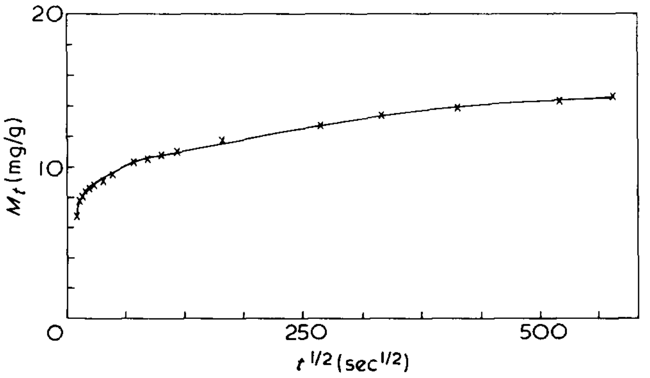

Figure 16 M_t vs. $t^{1/2}$ for sorption of n-hexane by polystyrene (0.534 μm powder) at 35°C, $P_{rel} = 0 \rightarrow 0.10$. X, Experimental; ——, equation (7) with $M_{\infty F} = 8.49$, $M_{\infty 1} = 1.95$, $M_{\infty,2} = 4.24$ mg/g, $k_F = 7.5 \times 10^{-3}$, $k_1 = 3 \times 10^{-4}$, $k_2 = 1 \times 10^{-5}$ sec^{-1}

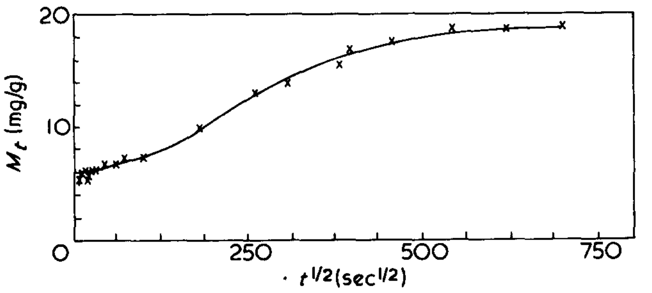

Figure 17 M_t vs. $t^{1/2}$ for sorption of n-hexane by polystyrene at 40°C, $P_{\mathrm{rel}} = 0.23 \rightarrow 0.50$. X, Experimental; ——, equation (7) with $M_{\infty F} = 5.93$, $M_{\infty 1} = 12.86$ mg/g; $k_F = 2 \times 10^{-2}$, $k_1 = 1.1 \times 10^{-5}$ sec^{-1}

which ultimately results in a time-dependent increase of free-volume to accommodate additional penetrant. The presaturation of pre-existing, available 'sites' in an incremental sorption experiment tends to increase the contribution of the ensuing relaxation processes relative to the contribution of rapid Fickian diffusion.

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