Superscripts

o = equilibrium
$+$ = transpose
i = initial

APPENDIX

One may write

$$dA_p = \left(\frac{\partial A_p}{\partial \xi_p}\right)_\zeta d\xi_p + \left(\frac{\partial A_p}{\partial \zeta}\right)_{\xi_p} d\zeta \tag{A1}$$

then,

$$\left(\frac{\partial A_p}{\partial \xi_p}\right)_{\mu_s} = \left(\frac{\partial A_p}{\partial \xi_p}\right)_\zeta + \left(\frac{\partial A_p}{\partial \zeta}\right)_{\xi_p} \left(\frac{\partial \zeta}{\partial \xi_p}\right)_{\mu_s} \tag{A2}$$

One also has

$$d\mu_s = \left(\frac{\partial \mu_s}{\partial \xi_p}\right)_\zeta d\xi_p + \left(\frac{\partial \mu_s}{\partial \zeta}\right)_{\xi_p} d\zeta \tag{A3}$$

and at constant μ_s,

$$\left(\frac{\partial \zeta}{\partial \xi_p}\right)_{\mu_s} = -\mathbf{a}^{-1} \left(\frac{\partial \mu_s}{\partial \xi_p}\right)_\zeta \tag{A4}$$

where $\mathbf{a}$ is given by Eq. 8. Substituting Eq. A4 into Eq. A2 and using the Maxwell relation, Eq. 6, one has

$$\left(\frac{\partial A_p}{\partial \xi_p}\right)_{\mu_s} = \left(\frac{\partial A_p}{\partial \xi_p}\right)_\zeta + \left(\frac{\partial Z}{\partial \xi_p}\right)_\zeta^{+} \mathbf{a}^{-1} \left(\frac{\partial \mu_s}{\partial \xi_p}\right)_\zeta \tag{A5}$$

Similarly

$$dZ = \left(\frac{\partial Z}{\partial \xi_p}\right)_\zeta d\xi_p + \left(\frac{\partial Z}{\partial \zeta}\right)_{\xi_p} d\zeta \tag{A6}$$

which yields

$$\left(\frac{\partial Z}{\partial \zeta}\right)_{A_p} = \left(\frac{\partial Z}{\partial \zeta}\right)_{\xi_p} + \left(\frac{\partial Z}{\partial \xi_p}\right)_\zeta \left(\frac{\partial \xi_p}{\partial \zeta}\right)_{A_p} \tag{A7}$$

From Eq. A1

$$\left(\frac{\partial \xi_p}{\partial \zeta}\right)_{A_p} = -\left(\frac{\partial A_p}{\partial \xi_p}\right)_\zeta^{-1} \left(\frac{\partial A_p}{\partial \zeta}\right)_{\xi_p} \tag{A8}$$

Using Eq. 6, Eq. A6 in Eq. A5 one has

$$\left(\frac{\partial Z}{\partial \zeta}\right)_{A_p} = \left(\frac{\partial Z}{\partial \xi_p}\right)_{\xi_p} + \left(\frac{\partial Z}{\partial \xi_p}\right)_\zeta \left(\frac{\partial A_p}{\partial \xi_p}\right)_\zeta^{-1} \left(\frac{\partial Z}{\partial \xi_p}\right)_\zeta^{+} \tag{A9}$$

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Part II: Anomalous Sorption

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Sorption of vapors in polymer membranes in the vicinity of and below the glass transition temperatures do not follow the Fickian (classical) diffusion. The reasons have been attributed to the molecular relaxation which affects both diffusivities and solubilities.

A time- and memory-dependent diffusion coefficient has been evaluated in Part I, in a form which is analogous to the treatment in the rheology of such materials. Together with a time-dependent solubility, the conservation equation for the sorption process has been solved. Two special cases are considered, where the relaxation times are short and where they are long. The results explain the anomalous behavior observed in the experiments. Comparison with the experiments has been made.

SCOPE

Mass transfer of small molecules in polymers is important in all stages. The kinetics of polymerization and polymer processing conditions are affected by it. Special features like dyeing and sorption of water vapor from the atmosphere are of great importance in the properties and the durability of polymeric fibers. Of importance in future is the use of polymer membranes

to separate vapor mixtures by permeation.

Analysis presented here deals with polymers in the vicinity of and below their glass transition temperatures. Presence of the small molecules in the glassy polymer imparts greater mobility to the system and gives rise to molecular relaxation. The diffusional process that results is anomalous, that is, cannot be quantitized with the usual ideas of mass transfer. A general formalism has been provided which contains the classical mass transfer process as a limiting case. Other limiting forms lead to a wide range of anomalous behaviors. These have been detected by experiments before. Quantitative analysis provided here is necessary not only for a better understanding, but also for the designing of dynamic systems, e.g., membrane separation processes.

CONCLUSIONS AND SIGNIFICANCE

The general treatment of viscoelastic diffusion during sorption process is characterized by a relaxation time. If the times of experiments are much greater than the relaxation time, the duffusion process tends to be the Fickian (classical) diffusion. This is the viscous limit. If the times of experiments are much smaller than the relaxation times, the elastic limit is reached. The solute penetrates the polymer as a concentration shock front travelling with a constant speed. These are Alfrey's shock waves.

Experiments are analyzed with the solutions presented for short and long relaxation times. The data that relaxation times are short are seen to be governed by the time dependence of the diffusivity rather than the time dependence of the solubility. Where the relaxation times are large, experiments confirm the theory.

The important contribution made here is the quantification of the process. The knowledge of the dynamics of diffusion of vapors through polymers is essential in designing membranes for the separation of vapor mixtures.

INTRODUCTION

One of the conventional experiments used to determine the diffusion coefficients of small penetrant molecules in polymers is the sorption method. It consists of giving a step change in the pressure of the gas or vapor permeant surrounding the polymer and measuring the change in the weight. The polymer sample is usually in form of a membrane of uniform thickness, $\ell \ll$ the major dimension of the face (Crank and Park, 1968).

Classical theory of diffusion, as given by Fick's law, predicts that the fractional mass uptake M_t/M_∞ is a function of $t^{1/2}/\ell$. Here M_t *and* M_∞ are mass uptakes at times t and at infinite time. A host of solute-polymer pairs satisfy this criterion (Fujita, 1968), even if the diffusion coefficients or the solubility coefficients are strong functions of concentrations. It also predicts a more restricted behavior that M_t/M_∞ is linearly proportional to $t^{1/2}$ at short times. This too is obeyed at short times.

Deviations start near the glass transition temperature of the polymer, T_g. Earlier, Meares (1958a,b) speculated that the diffusion coefficients at temperatures as high as 5 to 10°C higher than T_g is time-dependent. Later, investigators confirmed a specific type of anomalous diffusion in this region (Kishimoto and Matsumoto, 1959, 1964; Kishimoto and Enda, 1963; Odani, 1967). It was observed that M_t/M_∞ vs. $t^{1/2}/\ell$ plots were functions of ℓ as well, in contradiction to the results of the classical theory (Fujita, 1968).

A second type of anomaly was brought forth by Alfrey (1965). It was seen that M_t/M_∞ is a linear function of time t instead of $t^{1/2}$. It was also noted that the solute imbibition into the polymer is characterized by a sharp front advancing at constant speed. The region behind the front was a swollen gel with constant solute concentration. This behavior is observed below T_g and at moderately high solute activities.

Anomalous behavior may be anticipated below the glass transition temperature, because the system under those conditions may not be at thermodynamic equilibrium. For instance, it is well known that the properties of the glassy polymer depend on the rate at which it was cooled to temperatures below T_g. Its nonequilibrium state is also demonstrated by a tendency of the system to shift towards the equilibrium slowly (Kovacs, 1958). Slow cooling provides a means for bringing the glassy polymer to stay at equilibrium. It allows the polymer molecules some time to reorient itself towards the equilibrium state. Similar effects are seen in glassy polymer in presence of a species with low molecular weight. Its presence imparts enough mobility to allow a glassy polymer to attain a rubbery state. This is the well-known plasticizing effect (Bueche, 1962). Consequently, with the diffusion of the penetrant molecules, relaxation of the polymer takes place accompanied by a change in the properties. Not only will this affect the mobility of the polymer and along with it the diffusion coefficient, it will also affect the equilibrium uptake, that is, the solubility. One notes that in the use of classical theory of diffusion, it is assumed that the faces exposed to the surroundings are at equilibrium with the surroundings (Crank, 1968). Long and Richman (1960) in their experiments found that even though surrounding gas was maintained at constant pressure, the surface concentration was seen to change with time.

Thus, there is strong evidence that molecular relaxation does take place and affect the kinetics of sorption in the vicinity of and below T_g. However, there are also regions where they appear not to be influenced by the molecular relaxation. That is, a single constant diffusion coefficient is able to explain the sorption data, whatever the physico-chemical mechanism may be which leads to such a result. Such a behavior is seen when the solute is a permanent gas or when the sorption experiments are conducted with vapors at very low concentrations or at temperatures below T_g. These have been reviewed by Hopfenberg and Stannett (1973). It is felt that in such systems the molecular interactions are too small for a relaxation process to occur. That relaxation is not felt here, not due to the fact that it may not exist for these systems, but because the data have not been taken in the concentration-temperature region where such effects would dominate.

The above idea is derived from Alfrey's classic work (1965) where concentration of the penetrants vs. temperature diagrams were drawn to denote the various regions where different effects dominate. The idea was later explored in detail by Hopfenberg and Frisch (1969), and Vrentas, Jarzebski and Duda (1975). Far above T_g, the diffusion is classical. Far below T_g or for very low concentrations of the penetrant, the diffusion is also classical. Immediately above T_g, the diffusion is anomalous where M_t/M_∞ vs. $t^{1/2}/\ell$ plots are functions of ℓ. Below T_g and in the intermediate concentration ranges, the diffusion is anomalous, M_t/M_∞ being linear with time.

One needs to examine the anomalous diffusion in polymers in more detail. Hopfenberg and Stannet (1973) review the data (Kwei and Zupko, 1969, Frisch, Wang, and Kwei, 1969, Hopfenberg, Holley and Stannett, 1969, 1970, Baird, Hopfenberg, and Stannett, 1971) where the penetration of the solute is characterized by a sharp front advancing at constant speed. Behind the front is a swollen gel at a constant penetrant concentration. At the front osmotic pressure is assumed to convert the almost dry polymer into gel. Beyond the front is a small region where classical diffusion takes place. It is assumed that molecular relaxation takes place at the front. From the notions of classical diffusion, there is no concentration gradient behind the front and hence no driving force. However, there are strong gradients at the front and the driving forces are enormous there. It is known that the media which relax in time show memory-dependent transport coefficients (Fredrickson, 1974). The rate at which the memory fades depends (inversely) on the characteristic relaxation times. Consequently, if the relaxation times are long, a memory-dependent medium will remember almost perfectly that a front with a constant driving force has passed through. Thus, it would give rise to a flux at present time (when there is no driving force since it is behind the front), because such a medium remembers its past history. This is analogous to the argument given by Boltzman on the rheology of viscoelastic fluids (Fredrickson, 1974). Obviously, this state of affairs stops as the material relaxes and the memory fades. It is noteworthy that arguments cannot be presented under classical theory as to why the solute behind the front can move even though there is no concentration gradient.

To generalize the very diverse behaviors encountered, one might parameterize the rates with representative time scales, Vrentas and Duda (1979) thus find it necessary to characterize the diffusion in a polymer through a Deborah number, which is the ratio between relaxation time and the macroscopic diffusion time. Diffusion tends to be the classical form as Deborah number goes to zero. This is their viscous limit. As Deborah number becomes infinite, the diffusion again becomes classical for the polymer matrix does not change with time. This is their elastic limit. Viscoelastic behavior is seen in the intermediate regions. The time-dependent solubility is not considered. The search for the representation for a Deborah number leads them, like Alfrey et al. (1966) before them, to other transport properties. Ostensibly, a correlation exists among them; however, their correlation cannot be established. Here, a generalized treatment is attempted based on the diffusion and solubility coefficients obtained earlier (Neogi, 1982).

FORMULATION

The solubility is modelled in the sorption experiments with a time-dependent boundary condition; that is, concentration there is $C(t)$. Long and Richman (1960), Frisch (1964), and Neogi (1982) provide

$$C = c_i + (c_f - c_i)(1 - e^{-\beta t}). \tag{1}$$

Obviously if the rate of relaxation is rapid, β is large and $C \approx c_f$. Here c_i and c_f are the initial and final concentrations, respectively.

The generalized diffusion is modelled according to viscoelastic behavior (Fredrickson, 1974) as

$$j = -\int_o^t \mu(t - t')\frac{\partial c}{\partial x}(t',x)dt' \tag{2}$$

where μ is the diffusion relaxation function. Neogi (1982) has shown that

$$\mu(t) = D_i\delta(t) + \beta(D_o - D_i)e^{-\beta t} \tag{3}$$

where D_i and D_o are initial and final diffusivities and $\delta(t)$ is Dirac delta function.

The diffusion in polymers are strongly concentration-dependent (Alfrey, 1965; Hopfenberg and Frisch, 1969; Vrentas et al., 1975). An additional assumption that μ is independent of concentration is made. Hence in Eq. 2, it is necessary to make an assumption that the initial and final concentrations c_i and c_f of the step changes in the sorption experiments are very close. Then μ becomes independent of concentration, being evaluated c_f.

Some theorems in Laplace transforms are crucial in the developments that follow. The residue theorems give $\text{limit}_{p\to o}p\bar{f}(p) = \text{limit}_{t\to\infty}f(t)$, as well as $\text{limit}_{p\to\infty}p\bar{f}(p) = \text{limit}_{t\to o}f(t)$. It becomes apparent that the asymptotic solution for small p gives rise to an asymptotic solution for large t and vice versa. Further, the moments are given as

$$\int_o^\infty t^n f(t)dt = (-1)^n \frac{d^n}{dp^n}\bar{f}(p)\bigg|_{p=o}.$$

The convolutions in Eq. 2 are most easily handled through Laplace transforms. If

$$Lg(t) = \bar{g}(p)$$

and

$$Lf(t) = \bar{f}(p)$$

then $L \int_o^t f(t - t')g(t')dt' = \bar{g}\bar{f}$, where L denotes the Laplace transform; overbars, transformed quantities; and p, its variable. Taking the Laplace transform of Eq. 2 one has

$$\bar{j} = -\bar{\mu}\frac{d\bar{c}}{dx} \tag{4}$$

and

$$p\bar{j} = -\bar{\mu}\left(\frac{pd\bar{c}}{dx}\right). \tag{5}$$

Taking the limit $p \to o$ in Eq. 5, and using the residue theorems and the moment theorems, one has

$$j_\infty = -\left[\int_o^\infty \mu(t)dt\right]\left(\frac{dc}{dx}\right)_\infty \tag{6}$$

Here j_∞ and $(dc/dx)_\infty$ are the flux and the concentration gradient at steady state (reached at infinite times). Consequently, from Eq. 6, the steady-state diffusivity D_o is given by

$$D_o = \int_o^\infty \mu(t)dt \tag{7}$$

when such an integral exists.

If there is no memory effect, $\mu(t) = D_o\delta(t)$, where $\delta(t)$ is the Dirac's delta function. Substituting, in Eq. 5, noting that $\bar{\delta} = 1$,

$$\bar{j} = -D_o\frac{d\bar{c}}{dx}, \tag{8}$$

which on inversion gives the classical diffusion

$$j = -D_o\frac{\partial c}{\partial x}. \tag{9}$$

Relaxation functions μ are, therefore, distortions of the delta function of classical diffusion.

One needs to solve the conservation equation together with Eq. 2,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[\int_o^t \mu(t - t')\frac{\partial c}{\partial x}(t',x)dt'\right]\cdot \tag{10}$$

Eq. 10 is subject to the boundary conditions of symmetry

$$\frac{\partial c}{\partial x}\bigg|_{x=o} = 0 \tag{11}$$

and

$$c\big|_{x=\pm\ell/2} = C(t). \tag{12}$$

Here, $C(t)$ is the time-dependent solubility discussed earlier. It changes from the initial concentration c_i to a final concentration c_f. The initial condition is

$$c\big|_{t=o} = c_i. \tag{13}$$

Taking the Laplace transform of Eq. 10 subject to Eq. 13, we have

$$p\bar{c} - c_i = \bar{\mu}\,\frac{d^2\bar{c}}{dx^2}. \tag{14}$$

Eqs. 11 and 12 become

$$\left.\frac{d\bar{c}}{dx}\right|_{x=o} = 0 \tag{15}$$

and

$$\bar{c}|_{x=\pm\ell/2} = \overline{C} \tag{16}$$

The solution to Eqs. 14–15, is

$$\bar{c} = \left(\overline{C} - \frac{c_i}{p}\right)\frac{\cosh\left(x\sqrt{\dfrac{p}{\bar{\mu}}}\right)}{\cosh\left(\dfrac{\ell}{2}\sqrt{\dfrac{p}{\mu}}\right)} + \frac{c_i}{p}. \tag{17}$$

Further, as the mass uptake is

$$M_t = \int_{-\ell/2}^{\ell/2} (c - c_i)dx \tag{18}$$

as transformed quantities

$$\overline{M}_t = \int_{-\ell/2}^{\ell/2} \left(\bar{c} - \frac{c_i}{p}\right)dx. \tag{19}$$

The equilibrium mass uptake is

$$M_\infty = \ell(c_f - c_i) \tag{20}$$

Combining Eqs. 17–20,

$$\frac{\overline{M}_t}{M_\infty} = \frac{2}{\ell\sqrt{\dfrac{p}{\bar{\mu}}}}\,\frac{(p\overline{C} - c_i)}{p(c_f - c_i)}\tanh\left(\frac{\ell}{2}\sqrt{\frac{p}{\bar{\mu}}}\right). \tag{21}$$

For small p,

$$\frac{\overline{M}_t}{M_\infty} \sim \frac{1}{p} - \frac{\ell^2}{12D_o} \tag{22}$$

where the hyperbolic tangent has been expanded in series of the assumption that $p/\bar{\mu} \rightarrow o$ as $p \rightarrow o$. Further, the results that $p\overline{C} \rightarrow c_f$ and $\bar{\mu} \rightarrow D_o$ as $p \rightarrow o$ have been used. Equation 22 shows from the residue theorem that $\text{limit}_{p\rightarrow o} p\overline{M}_t/M_\infty = \text{limit}_{t\rightarrow\infty} M_t/M_\infty = 1$. Using the moment theorem one has

$$\lim_{t\rightarrow\infty}\int_o^t \left(\frac{M_t(t')}{M_\infty} - 1\right)dt' = \lim_{p\rightarrow o}\left(\frac{\overline{M}_t}{M_\infty} - \frac{1}{p}\right) = -\frac{\ell^2}{12D_o}.$$

It provides a means for estimating D_o from the behavior at infinite times when the concentration variations are negligibly small. Thus, D_o is the zero-flux diffusivity. Equation 21 reduces to the correct limit of $M_t/M_\infty \rightarrow o$ as $t \rightarrow o$ on using the residue theorem and the assumption that $p/\sqrt{\bar{\mu}} \rightarrow \infty$ as $p \rightarrow \infty$. From Eqs. 1 and 3,

$$\overline{C} = \frac{c_i}{p} + (c_f - c_i)\left[\frac{1}{p} - \frac{1}{p+\beta}\right] \tag{23}$$

and

$$\bar{\mu} = D_i + \beta\frac{(D_o - D_i)}{(p + \beta)}. \tag{24}$$

The inversion of Eq. 21 is accomplished by noting that there are simple poles at $p = 0$, $\ell/2\sqrt{p/\bar{\mu}} = i(k + 1/2)\pi$ and at $p = -\beta$. The inversion is

$$\frac{M_t}{M_\infty} = 1 - e^{-\beta t} + \frac{8\beta}{\ell^2}\sum_{k=1}^{\infty}\frac{1}{p_k(p_k + \beta)}\cdot\frac{e^{p_k t}}{\left(\dfrac{d}{dp}\dfrac{p}{\bar{\mu}}\right)_{p=p_k}}. \tag{25}$$

Here p_k is given by

$$\frac{p_k}{\bar{\mu}(p_k)} = -(2k + 1)^2\frac{\pi^2}{\ell^2}. \tag{26a}$$

Combining Eqs. 24 and 26a,

$$p_k = -\frac{1}{2}\left[\beta + (2k + 1)^2\frac{\pi^2 D_i}{\ell^2}\right] \pm \frac{1}{2}\sqrt{\left\{\left[\beta + (2k + 1)^2\cdot\frac{\pi^2 D_i}{\ell^2}\right]^2 - 4\beta D_o(2k + 1)^2\frac{\pi^2}{\ell^2}\right]} \tag{26b}$$

where it can be seen that $p_k < 0$ for all k.

Equations 24, 25 and 26b provide the general solution to the problem of anomalous sorption, but limiting cases need to be studied separately. This is not only to explain the diverse types of anomalies encountered in the experiments, but also to cover certain cases where the representation of the fractional mass uptake in Eq. 25 does not illustrate adequately the nature of the process.

EFFECTS OF RELAXATION TIME

Relaxation time is given by β^{-1}. When $\beta = \infty$, the relaxation is instantaneous, and Eqs. 25 and 26b reduce to

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{k=1}^{\infty}\frac{e^{-(2k+1)^2\pi^2 D_o t/\ell^2}}{(2k + 1)^2} \tag{27}$$

which is a well-known result of classical sorption (Crank, 1965).

If the relaxation time is not very small, rearranging Eq. 24

$$\frac{p}{\bar{\mu}} = \frac{p(p + \beta)}{pD_i + \beta D_o} \tag{28}$$

where on letting $\beta \gg p$,

$$\frac{p}{\bar{\mu}} = \frac{p\beta}{pD_i + \beta D_o}. \tag{29}$$

(Note that, if on addition $\beta D_o \gg pD_i$, Eq. 27 will be obtained eventually.) Combining Eqs. 26a and 29

$$p_k = -\frac{(2k + 1)^2\pi^2 D_o/\ell^2}{1 + (2k + 1)^2\pi^2 D_i/\beta\ell^2}. \tag{30}$$

Equations 29 and 30 may now be substituted into Eq. 25 to obtain the solution as

$$\frac{M_t}{M_\infty} = 1 - e^{-\beta t} - \frac{8}{\pi^2} \times \sum_{k=1}^{\infty}\frac{e^{-\frac{(2k+1)^2\pi^2 D_o t/\ell^2}{1 + (2k+1)^2\pi^2 D_i/\beta\ell^2}}}{\left[1 - \dfrac{(2k + 1)^2\pi^2(D_o - D_i)}{\beta\ell^2}\right](2k + 1)^2}. \tag{31}$$

In Eq. 30, one notes that the diffusion coefficient is attenuated from its classical value of D_o to $D_o/[1 + (2k + 1)^2\pi^2 D_i\beta\ell^2]$. It is also seen in Eq. 31 that plots of M_t/M_∞ vs. $t^{1/2}/\ell$ will be functions of ℓ.

One may now consider the case when the relaxation times are very large, or β very small. Thus neglecting terms in β in Eq. 28,

$$\frac{p}{\bar{\mu}} = \frac{p}{D_i}. \tag{32}$$

In this case the sorption becomes classical, with D_i substituted for D_o in Eq. 27.

An interesting case is obtained when β is small and D_i is negligible. Equation 28 becomes

$$\frac{p}{\bar{\mu}} = \frac{p^2}{\beta D_o}. \tag{33}$$

On analyzing Eqs. 33 and 26a, it is seen that p_k in this case is purely imaginary. Understanding of as to why this happens can be reached by substituting for $\bar{\mu}$ from Eq. 33 into the basic conservation equation (Eq. 14), one obtains

$$p^2\bar{c} - pc_i = \beta D_o\frac{d^2\bar{c}}{dx^2} \tag{34a}$$

which on inversion yields

$$\frac{\partial^2 c}{\partial t^2} = \beta D_o \frac{\partial^2 c}{\partial x^2}. \tag{34b}$$

Equation 34b is a shock wave equation which is expected to yield a solution different in nature from the solution of a diffusion equation. Before attempting a solution in Eq. 34a, a physical interpretation of this approximation needs to be given. It is seen in Eq. 3 if D_i is negligible, permeation of the solute takes place into the polymer only because of relaxation. The solution to Eq. 34a is obtained in the Appendix; the profile is

$$c = c_i + (c_f - c_i)\left[\mathcal{H}\left(t + \frac{x - \ell/2}{\sqrt{\beta D_o}}\right) + \mathcal{H}\left(t - \frac{x + \ell/2}{\sqrt{\beta D_o}}\right)\right] \quad \text{for } t < \frac{\ell}{2\sqrt{\beta D_o}}$$

$$= c_f \quad \text{for } t \geqslant \frac{\ell}{2\sqrt{\beta D_o}}. \tag{35}$$

Here $\mathcal{H}$ is the Heavyside step function. From left to right, the profile is given by a constant concentration c_f, with a step down to c_i at $x = -\ell/2 + t\sqrt{\beta D_o}$ and a step up to c_f at $x = \ell/2 - t\sqrt{\beta D_o}$. Thus there are two shock waves advancing towards the center with constant velocities of $\sqrt{\beta D_o}$. Obviously these are Alfrey's shock fronts.

The fractional mass uptake is given as

$$\frac{M_t}{M_\infty} = \frac{2\sqrt{\beta D_o}}{\ell}t \quad \text{for } t < \frac{\ell}{2\sqrt{\beta D_o}}. \tag{36}$$

$$= 1 \quad \text{for } t \geqslant \frac{\ell}{2\sqrt{\beta D_o}}$$

Thus in this case $M_t/M_\infty \propto t/\ell$.

EFFECT OF TIME

It has been observed before that the solution at large values of time t in its Laplace transform is equivalent to solution for small p, and vice versa.

Thus at large t, or small p, $p < \beta$, Eq. 27 is obtained at very large times ($p \ll \beta$) and Eq. 31 is obtained at moderately large times ($p < \beta$). At small t, or large p, $p \gg \beta$, classical diffusion with diffusion coefficient of D_i or Alfrey's shock waves (Eq. 36) when $D_i \approx 0$ is obtained. Therefore, large times give the same results as small relaxation times. One should analyze the quantity (βt) which is large both when the relaxation time β^{-1} is small and when t is large. Similarly (βt) is small when the relaxation time β^{-1} is large or t is small. Consequently, it is the magnitude of (βt) which unifies the two systems of approximation. This result is quite analogous to the rheology of viscoelastic materials (Fredrickson, 1974).

COMPARISON WITH EXPERIMENTS

Halftimes are defined as $t = t_{1/2}$ where $M_t/M_\infty = \frac{1}{2}$. Halftimes $t_{1/2}$ (with a constant multiplying factor) have been plotted against ℓ^2 in Figures 1(a) and (b). Each set of data have been taken under identical conditions with ℓ^2 as a variable. If the diffusion were classical, straight lines through the origin would have been expected. In the limit $\ell^2 \rightarrow 0$, Eq. 25 becomes

$$\frac{M_t}{M_\infty} = 1 - e^{-\beta t}$$

$$\text{or } t_{1/2}|_{l=0} = \frac{\ell n 2}{\beta}. \tag{37}$$

The two plots have been extrapolated to the origin for simplicity; however, it is apparent that a small positive intercept—$t_{1/2}|_{l=0}$—should exist. That is, the system has a large β or small relaxation time.

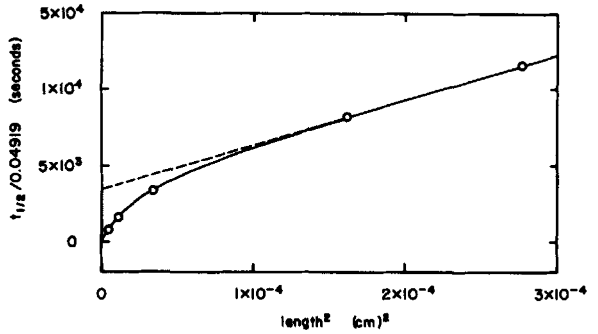

Figure 1a. Data of Odani (1967) plotted for absorption of methyl ethyl ketone in actactic polystyrene at 25°C and step up from vacuum to 1.44 × 10² Pa. Half-times $t_{1/2}$ are plotted against ℓ^2. The asymptote, Eq. 38c has been shown with dashes. The system is *above* its T_g by less than 15°C.

From this, one has the appropriate equation, in these cases as Eq. 31. Neglecting the second term on the righthand side for large β,

$$\frac{1}{2} \simeq 1 - \frac{8}{\pi^2}\exp\left[-\frac{\pi^2 D_o t_{1/2}/\ell^2}{1 + \pi^2 D_i/\beta\ell^2}\right] \tag{38a}$$

where (a) only p_1 has been included and higher p_k have been neglected under the assumption that $p_k t_{1/2}$ for $k > 1$ are large and negative; consequently, the terms $\exp(p_k t_{1/2})$ may be neglected; (b) the term $[1 - \pi^2(D_o - D_i)/\beta\ell^2]$ has been approximated to 1, under the assumption that $D_i \approx D_o$ and β is known to be large. Equation 38a simplifies to

$$\frac{t_{1/2}}{0.04919} \cong \frac{\pi^2 D_i}{D_o \beta} + \frac{\ell^2}{D_o}. \tag{38b}$$

With the previous assumption that $D_i \approx D_o$,

$$\frac{t_{1/2}}{0.04919} \cong \frac{\pi^2}{\beta} + \frac{\ell^2}{D_o} \tag{38c}$$

It may be noted that ℓ^2/D_o is the macroscopic time scale of the experiment. Thus, for the relaxation time to be considered small, ℓ^2 should be large; that is, Eq. 38c is the asymptotic form for large ℓ^2. The lefthand side of Eq. 38c has been plotted against ℓ^2 in Figures 1(a) and (b). Equation 38c asymptotes have been drawn. In Figure 1(a), $D_o = 10^{-11}$ m²/s and $\beta = 9.12 \times 10^{-3}$ s^{-1}. The value of β appears to be very small, although from previous discussions it should have been large. However, the values yield the relaxation time β^{-1} as 110 s in relation to the macroscopic diffusion times as $\ell^2/D_o \sim 1{,}000$ s; thus, Figure 1(a) does correspond to the case of small relaxation times (or "large" β) as assumed earlier.

Similarly in Figure 1(b), $D_o = 1.31 \times 10^{-15}$ m²/s and $\beta = 2.62 \times 10^{-15}$ s^{-1}. The relaxation times β^{-1} is 3.82×10^4 s and the diffusion times $\ell^2/D_o \sim 10^6$ s. Consequently, this too is a case of small relaxation times.

The data of Hopfenberg, Holley and Stannett (1969, 1970) and Baird, Hopfenberg and Stannett (1971) are striking in that the

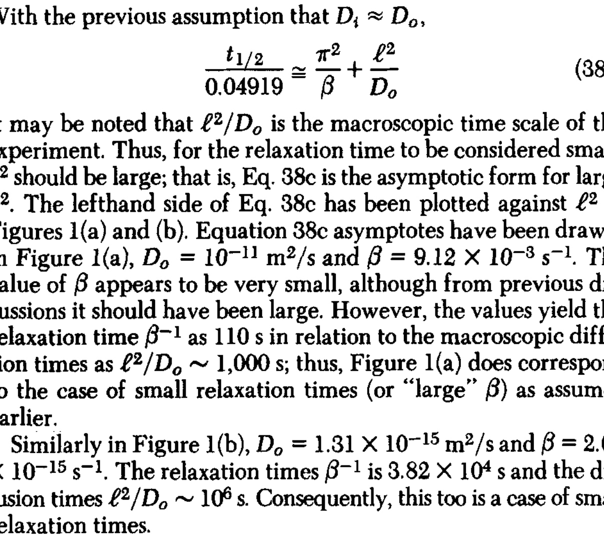

Figure 1b. Data of Kishimoto and Matsumoto (1964) plotted for absorption of allyl chloride in polyvinyl acetate at 40°C and step up from vacuum to 1.56 × 10² Pa. Half-times $t_{1/2}$ are plotted against ℓ^2. The asymptote, Eq. 38c has been shown with dashes. The system is *above* its T_g by less than 15°C.

TABLE 1. βD_o VALUES

System	βD_o cm^2·s^{-2}	Temp. °C	Pres. Pa × 10^{-4}
Biaxially	2.46×10^{-8}	25	6.2
Oriented	2.04×10^{-8}	30	6.2
Polystyrene	1.7×10^{-8}	35	6.2
	3.88×10^{-8}	30	7.33
	9.92×10^{-8}	30	5.2
Cast Annealed	6.44×10^{-9}	30	6.2
Polystyrene	5.08×10^{-9}	35	6.2
	8.39×10^{-9}	30	7.33

fractional mass uptake $M_t/M_\infty \propto t$ and at $M_t/M_\infty = 1$ they turn the corner sharply as seen in Eq. 36. When $M_t/M_\infty = 1$, $t = t_1 = \ell/2\sqrt{\beta D_o}$. The data of Hopfenberg, Holley and Stannett (1969, 1970) have been analyzed, and βD_o values are listed in Table 1.

Data of Baird et al. (1971) show a peculiarity. Instead of a sharp corner at $M_t/M_\infty = 1$, there is a small peak. This overshoot is small and decays rapidly. It can be seen that when M_t/M_∞ reaches 1, two Alfrey concentration shock fronts clash at the center giving rise to oscillations. The disturbances die rapidly, possibly because the system is forced to equilibrate with the surroundings.

The data where diffusion is classical even though anomalous effects are expected (Vrentas and Duda, 1978) have not been analyzed. The apparent diffusion coefficient there is its initial value D_i and not its equilibrium value D_o.

DISCUSSION

Diverse behaviors that are seen experimentally can be predicted from the theory. A method of classification has been attempted by Vrentas, Jarzebski and Duda (1975). They define a Deborah number which is the ratio of the relaxation time to the macroscopic diffusion time. As mentioned previously, they arrive at the numbers through correlations with properties other than diffusional relaxation. It is not necessary here to go outside the diffusional effects to seek a representation for Deborah number, it is simply $\beta^{-1}/(\ell^2/D_o)$. Vrentas et al. (1975) argue on physical grounds that classical diffusion should be obtained both when the ratio is very small or very large. This has been demonstrated here. However, they also argue that when the Deborah number ~1, the anomalous effects (Alfrey's shockwaves) are most pronounced. It is here that difficulties arise as anticipated by Vrentas and Duda (1979) and Vrentas, Jarzebski and Duda (1975). It is seen that Alfrey's shockwaves are generated by wave equation, Eq. 34b, and not by diffusion equation. Consequently, the existence of D_o, if it does at all exist, is irrelevant to the process, and so is a Deborah number as defined previously.

However, it has been shown that the magnitude of (βt) can provide a sufficient indication as to which way the process will go.

(βt) (i) Very Small: Classical (D_i)
(ii) Small: Alfrey Shockwaves
(iii) Moderately Large: M_t/M_∞ vs. $t^{1/2}/\ell^2$ plots are functions of ℓ
(iv) Very Large: Classical (D_o)

It also shows correctly that an entire sorption process goes through all these four stages, although the magnitude of β is usually such to make the contribution to only one stage significant. It is noteworthy that $(\beta t_{1/2})$ conforms to the definition of inverse Deborah number.

It is also noteworthy that the diffusion coefficients in the systems analyzed here are usually taken to be strongly dependent on the concentrations (Fujita, 1968; Park, 1968). However, in the theory presented here, the diffusion coefficients have been assumed to be independent of concentration. In spite of that, the agreement between the theory and the experiments appear to be excellent, at least in the range of variables studied.

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NOTATION

c = concentration
C = time-dependent solubility expressed as time-dependent equilibrium concentration
D_o = zero flux diffusion coefficient
$\mathcal{H}$ = Heavyside step function
i = $\sqrt{-1}$
j = diffusive flux
ℓ = membrane thickness
L = Laplace transform
M = mass uptake
p = variable of Laplace transform
t,t' = time and its dummy variable in the time integrals
$t_1,t_{1/2}$ = times at $M_t/M_\infty = 1$ and ½
x = coordinate in the direction of flux

Greek Letters

β = inverse relaxation time, Eqs. 1 and 3
δ = Dirac delta function
μ = diffusion relaxation function, Eqs. 2 and 3

Subscripts

i = initial
o,f = final
t = at time t
∞ = at infinite time
k = kth value
n = nth value

Symbols

— = Laplace transformed qualities

APPENDIX

The solution to Eq. 34a for the sorption case subject to symmetry and $\bar{c}|_{x=\pm\ell/2} = c_f/p$ is

$$\bar{c} = \frac{c_i}{p} + \frac{(c_f - c_i)}{p} \frac{\cosh(xp/\sqrt{\beta D_o})}{\cosh\left(\frac{\ell}{2}p/\sqrt{\beta D_o}\right)} \tag{A1}$$

Since it is known that the solution is discontinuous, an attempt is made to obtain the solution as a sum of discontinuous steps. Thus, hyperbolic cosines in Eq. A1 are rewritten as exponentials and the denominator expanded to give

$$\bar{c} = \frac{c_i}{p} + \frac{(c_f - c_i)}{p}\left[\exp\left(\frac{x - \ell/2}{\sqrt{\beta D_o}}p\right) + \exp\left(-\frac{x + \ell/2}{\sqrt{\beta D_o}}p\right) + \sum_{k=1}^{\infty}\exp\left(\frac{x - k\ell}{\sqrt{\beta D_o}}p\right) + \sum_{k=1}^{\infty}\exp\left(-\frac{x + k\ell}{\sqrt{\beta D_o}}p\right)\right]$$

and inverted to give

$$c = c_i + (c_f - c_i)\left[\mathcal{H}\left(t + \frac{x - \frac{\ell}{2}}{\sqrt{\beta D_o}}\right) + \mathcal{H}\left(t - \frac{x + \frac{\ell}{2}}{\sqrt{\beta D_o}}\right) + \sum_{k=1}^{\infty}\mathcal{H}\left(t + \frac{x - k\ell}{\sqrt{\beta D_o}}\right) + \sum_{k=1}^{\infty}\mathcal{H}\left(t - \frac{x + k\ell}{\sqrt{\beta D_o}}\right)\right] \tag{A2}$$

All the terms in the summation are zero *inside the membrane* for $t = t_1 \leqslant \ell/2\sqrt{\beta D_o}$, whence

$$c = c_i + (c_f - c_i)\left[\mathcal{H}\left(t + \frac{x - \dfrac{\ell}{2}}{\sqrt{\beta D_o}}\right) + \mathcal{H}\left(t - \frac{x + \dfrac{\ell}{2}}{\sqrt{\beta D_o}}\right)\right] \quad \text{for } t < \frac{\ell}{2\sqrt{\beta D_o}},$$

$$= c_f \quad \text{for } t = t_1 = \frac{\ell}{2\sqrt{\beta D_o}} \tag{A3}$$

One is not interested beyond that. For $t < \ell/2\sqrt{\beta D_o}$, Eq. A3, from left to right, shows the concentration profile at a constant concentration c_f, stepping down to c_i at $x = \sqrt{\beta D_o} - \ell/2$, stepping up to c_f at $x = \ell/2 - \sqrt{\beta D_o}t$. Obviously the two steps meet at $t = t_1$. Equation 43 readily follows.

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