Mass Transport with Relaxation in Polymers

The non-Fickian mass transport behavior observed in polymeric materials is here analyzed through a viscoelastic constitutive equation for the diffusive flux, endowed with concentration-dependent relaxation time and diffusivity. The present model thus overcomes the limitations shown by Neogi's model and by the Cattaneo equation used by Camera-Roda and Sarti. In addition to the Fickian behaviors at both small and high Deborah numbers, the model accounts for case II behavior and anomalous diffusion at intermediate Deborah number, possibly with the presence of a shock wave in the concentration profile which moves at a concentration-dependent velocity. Weight uptake accelerations and overshoots are also accounted for at intermediate Deborah numbers. The dimensionless problem has been numerically solved and the role of the relevant dimensionless parameters is discussed for both sorption and desorption.

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Introduction

In transport processes, an instantaneous response of the flux to a change in the driving force is implied by the formulation of the classical Fick's and Fourier's laws. However, this representation of the physical mechanism is somehow far from the physical sensibility, even if it is a good representation of many common transport phenomena. Actually, in thermal conduction it has been shown that heat should be modeled as moving with a high but finite propagation speed (Cattaneo, 1948; Vernotte, 1958; Weyman, 1967), while various considerations (Neogi, 1983a; Neogi et al., 1986; Kim and Neogi, 1984; Ocone and Astarita, 1987) suggest that mass diffusion in a solid medium is limited by the characteristic times of molecular or stress rearrangements and morphological changes.

Usually, in such cases the crude, final formulation of the problem resorts to a particular form of the constitutive equation for the flux, where a term appears to endow the flux with a relaxation with a characteristic relaxation time. An effect of this approach to the problem is that the model may exhibit hyperbolic peculiarities, namely the onset of moving waves of temperature or concentration and the oscillations of heat or mass content around a final equilibrium value.

In mass sorption in polymers, use has been made of the former formulation to represent the "anomalous" non-Fickian behavior that is experimentally observed under certain conditions. Consistent with the rheology of viscoelastic materials, Neogi (1983b) introduced a constitutive equation for the diffusive flux that accounts for a relaxation with a characteristic time τ from initial to final Fickian behaviors, with very different diffusivities D_i and D_0. Results in terms of mass uptake vs. time appear to reproduce qualitatively some particular aspects of anomalous sorption (Adib and Neogi, 1987), even if they were obtained under the restrictive assumption of independency of the physical properties on composition. Relaxation time and diffusivity varying with the solvent concentration were earlier assumed by Camera-Roda and Sarti (1986), who adopted a constitutive equation analogous to that proposed in thermal problems by Cattaneo (1948) and Vernotte (1958), resorting to a hyperbolic system of differential equations of change. Both the resulting concentration profiles, which show a moving front with variable velocity, and the overshoot of mass uptake with respect to the equilibrium value are typical of some experimentally observed behaviors (Kambour et al., 1966; Mercier et al., 1967; Titow et al., 1974; Overbergh et al., 1975; Lyubimova and Frenkel, 1984; Vrentas et al., 1984). In some cases the results of the model by Neogi, as well as of the model by Camera-Roda and Sarti, show, after an overshoot in the weight uptake, oscillations in the penetrant content which rapidly fade away with time. Numerically that behavior is clearly visible, although there is so far no clearcut experimental evidence either in favor or against the occurrence of such oscillations.

It must be observed that when constancy of the material properties is assumed as in the model by Neogi, a concentration

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shock front cannot form if the solubility at the penetrant-polymer interface is allowed to relax from an initial value to a final equilibrium value while only smooth concentration profiles are reproduced. However, a sharp concentration profile is experimentally detected even when relaxation of the interface solubility takes place (Long and Richman, 1960; Laski, 1986). Furthermore, in the case in which Neogi's formulation can accommodate concentration shock waves, that is, under Riemann jump initial conditions, the shock waves are endowed only with a constant amplitude as well as with a constant propagation speed, contrary to what was experimentally observed in many cases (Nicolais et al., 1977; Thomas and Windle, 1981). This indicates the qualitative importance of accounting for concentration dependence of relaxation time and diffusivity. On the other hand, the memory function for the diffusivity used in Neogi's work, although characterized by a sound behavior, nonetheless allows for the relaxation from an initial value D_i to a final value D_0 based only on the observation time length, irrespective of the concentration level or history that has been experienced. In such an approach it is thus conceivable that some material points have relaxed to a final value D_0 even though no appreciable penetrant concentration has been reached, which is contrary to the usual understanding. Moreover, the use of concentration-dependent physical properties enables one to overcome the difficulties that are encountered in the use of Neogi's formulation in sorption-desorption cycles, due to the need for an arbitrary and ad hoc swap of D_0 for D_i and vice versa when the direction of the mass flux is changed.

On the other side, the pure hyperbolic formulation, albeit with concentration-dependent parameters, may lead to serious physical inconsistencies. Indeed, since the relaxation time increases with decreasing penetrant concentration, there are relaxation times for which the mass flux does not significantly fade away irrespective of the vanishing concentration gradient. Therefore, during desorption the hyperbolic model could give rise to high outer fluxes even when the penetrant content is small, thus leading ultimately to negative concentration values. Besides, the experimental evidence of a Fickian precursor to the concentration shock front is disregarded by the hyperbolic model.

The aim of the present work is to enhance the model of Camera-Roda and Sarti (1986) in order to investigate both sorption and desorption in polymers by adopting a modified derivative expression of the constitutive equation proposed by Neogi (1983b) with a proper dependency of physical properties on penetrant concentration. In such a way a rather simple model is improved with some relevant qualitative features:

1. A rather sharp concentration front may form even when the solubility relaxes at the penetrant-polymer interface
2. Under relaxation controlled conditions, the shock waves in the concentration profile propagate at a speed that is not a constant but rather is concentration dependent
3. The apparent diffusivity relaxes to its proper value both in sorption and in desorption as well as in differential or incremental sorption steps
4. The oscillations after the overshoot are indeed much less important
5. The physical inconsistency resulting in the desorption process with a purely hyperbolic model is overcome
6. The onset of the Fickian precursors to the sharp concentration fronts is obtained.

Mathematical Formulation

Despite the complexity of solvent penetration in polymers, due to the coupling of stress, concentration, and chemical potential fields (Kim and Neogi, 1984; Durning and Russel, 1985; Neogi et al., 1986; Ocone and Astarita, 1987; Doghieri et al., 1988; Carbonell and Sarti, 1990), a reasonable continuum formulation of the problem could be obtained using just the solvent conservation law and lumping the relaxation properties that are observed into the constitutive equation for the diffusive flux. So the diffusive flux may be expressed as the sum of some terms, every one endowed with a proper relaxation time. This treatment may be justified by considering that the final observable response of the flux is also due to a relaxation accompanying the viscoelastic stress or molecular rearrangements that take place on various time scales in polymeric materials near and below the glass transition temperature.

The simplest convenient and likely constitutive equation ffr the diffusive flux could be considered the sum of just two terms: one, J_f, which encompasses a vanishing relaxation time, that is, a Fickian term, and the other, J_r, with a finite relaxation time resorting to the form already investigated by Camera-Roda and Sarti (1986). Accordingly, here it has formally been assumed for the volumetric diffusive flux:

$$J = J_f + J_r \tag{1}$$

with

$$J_f = -D_f \operatorname{grad} \varphi \tag{2}$$

$$J_r = -D_r \operatorname{grad} \varphi - \tau \mathcal{D} J_r / \mathcal{D} t \tag{3}$$

In Eq. 3 the time derivative of J_r must be an objective material time derivative. Indeed the bulk and polymer velocity field may not be negligible (Sarti et al., 1986; Durning and Tabor, 1986); however, for the sake of simplicity, in the following we will confine our attention to the cases in which the bulk velocity field may be neglected. In this way the implications of just the diffusive flux given by the present formulation are investigated and a direct comparison with other existing models may be obtained. Thus Eq. 3 will be approximated by

$$J_r = -D_r \operatorname{grad} \varphi - \tau\, \partial J_r / \partial t \tag{4}$$

The governing balance equations, when written in terms of the volume fraction of penetrant φ and of the volumetric fluxes J, J_f, and J_r, result in:

$$\partial \varphi / \partial t = -\operatorname{div} J \tag{5}$$

together with the proper initial and boundary conditions that will be examined later.

It is worth noting that thus far the formulation is completely equivalent to Neogi's model when $D_r = D_0 - D_i$ and $D_f = D_i$. It is also apparent, by considering the corresponding integral formulation, that the mathematical aspect of the present model resembles those proposed by Durning and Tabor (1986) and by Jäckle and Frisch (1985), which were derived based on an analysis of molecular relaxation.

In order to properly accommodate a relaxation from an initial

Fickian behavior to a final one with different diffusivities, the following expressions of D_r and D_f are considered:

$$D_r = D_\infty(\varphi) - D_{in} \quad (6)$$

$$D_f = D_{in} \quad (7)$$

Here D_{in} represents the diffusivity at the very beginning of a diffusion process, or when a change occurs from a steady-state situation.

The dependence of D_∞ and τ on φ may be assumed exponential according to many empirical expressions (Long, 1965; Aptel et al., 1974; Greenlaw et al., 1977; Stern and Saxena, 1980; Néel et al., 1985; Aptel and Néel, 1986), which for most practical cases are approximately consistent with the free volume theory (Fujita, 1961; Fels and Huang, 1970, 1971; Fang et al., 1975). It follows that:

$$D_\infty(\varphi) = D_{eq} \exp[g(\varphi - \varphi_{eq})] \quad (8)$$

$$\tau(\varphi) = \tau_{eq} \exp[K(\varphi_{eq} - \varphi)] \quad (9)$$

where D_{eq} and τ_{eq} represent, for $\varphi = \varphi_{eq}$, the diffusivity and the relaxation time, respectively. The quantity φ_{eq} is understood to indicate the penetrant volume fraction at equilibrium with pure penetrant in the external environment.

If the diffusivity in the unpenetrated polymer D_i is introduced, Eq. 8 is modified as follows:

$$D_\infty(\varphi) = D_i (D_{eq}/D_i)^{(\varphi/\varphi_{eq})} = D_i \exp[g\varphi] \quad (10)$$

since the ratio D_{eq}/D_i can be expressed as $D_{eq}/D_i = \exp[g\varphi_{eq}]$.

Some remarks on the preceding equations are now in order.

1. Integration in time of the constitutive equation reduces to the expression in Neogi (1983b) and Adib and Neogi (1987) only if τ, D_f, D_r are taken constant.

2. The diffusion mechanism is non-Fickian; however, the process could be considered to take place according to an instantaneous Fickian diffusive flux with an effective diffusivity changing with time. In fact at very early times of the diffusion process the diffusivity is D_{in} and relaxes with time toward another Fickian diffusion in which $D_\infty(\varphi)$ holds (Adib and Neogi, 1987). Since from Eq. 10 $D_\infty(0) = D_i$, it follows that D_i should be considered an intrinsic diffusivity of the unpenetrated polymer matrix. Analogously, D_{eq} represents the diffusivity $D_\infty(\varphi_{eq})$ of the completely relaxed polymer at equilibrium with pure penetrant in the external environment.

3. The resulting system of partial differential equations is parabolic, even if, when D_f/D_r tends to 0, it admits as a borderline case the hyperbolic problem already investigated by Camera-Roda and Sarti (1986) for the sorption process.

4. τ depends on the solvent concentration as a consequence of the plasticizing effect produced by the penetrant. In any case, the exponential factor K in Eq. 9 should be taken different from the exponential factor g in Eq. 8 for the diffusivity D_∞. Approximately, D_∞ should vary with the reciprocal of the shear viscosity whereas τ should vary with the ratio of the viscosity to the shear modulus (Ferry, 1970), both these quantities being affected at different extents by the penetrant concentration.

5. The previous equations hold effective both for sorption and desorption, whereas Neogi's formulation is consistent with initial and final diffusivities only for the sorption process and consequently there are problems in describing sorption-desorption cycles.

The mathematical model considered here is thus represented by the balance equation, Eq. 5, and by the constitutive assumptions given by Eqs. 1, 2, and 4 in which the physical parameters are expressed through Eqs. 6–10. The problem is always parabolic in nature and reduces to a hyperbolic system in the limit of $D_f \ll D_r$. The initial conditions must be given in terms of both the penetrant volume fraction and the volumetric flux. The boundary conditions are represented by the value of the penetrant volume fraction at the penetrant-polymer interface I. Although in most cases equilibrium concentration is assumed to hold at the boundary, here consistency with the existence of relaxation processes must be accounted for; thus solubility relaxation will be allowed along the lines indicated first by Long and Richman (1960), and according to the results of Petropoulos (1984), Durning and Tabor (1986), and Laski (1986). At the penetrant-polymer interface it is then written:

$$\varphi = \varphi_w \quad \text{at } t = 0 \quad \text{on } I \quad (11)$$

$$\tau \frac{d\varphi}{dt} = \varphi_{\text{fin}} - \varphi \quad \text{at } t > 0 \quad \text{on } I \quad (12)$$

where the relaxation time τ is taken to be the same as the flux relaxation time given by Eq. 9, consistent with Neogi (1983a). In Eq. 12 the quantity φ_{fin} is the final equilibrium value with the external environment. The boundary conditions given through Eqs. 11 and 12 need the specification of an initial value φ_w.

In the current scheme the distinction of sorption from desorption follows from the different relevant initial and boundary conditions as well as from the different values of D_{in} in the two processes. In addition to Eq. 11, the typical initial conditions that have been analyzed in the numerical solution are as follows:

$$\varphi = \varphi_{in};\ J = 0 \text{ in the bulk of the polymer and } t = 0 \quad (13)$$

$$J = 0$$

$$\text{at the polymer-penetrant solution interface and } t = 0 \quad (14)$$

The values of the intervening parameters φ_{in}, φ_w, and φ_{fin} for the sorption and desorption cases are given as follows:

Sorption into dry polymer

$$\varphi_{in} = 0 \quad (15)$$

$$\varphi_w = 0.8\,\varphi_{eq} \quad (16)$$

$$\varphi_{fin} = \varphi_{eq} \quad (17)$$

Desorption from equilibrium swelling to dry polymer

$$\varphi_{in} = \varphi_{eq} \quad (18)$$

$$\varphi_w = 0.2\,\varphi_{eq} \quad (19)$$

$$\varphi_{fin} = 0. \quad (20)$$

Furthermore, in the present computations the initial diffusivity D_{in} has been taken to be D_i (diffusivity of unpenetrated polymer matrix) and D_{eq} (diffusivity of completely relaxed polymer at equilibrium) for sorption and desorption, respectively. According to the previous observation regarding the non-Fickian/Fickian character of the diffusion and to the assumed boundary conditions, this implies that in sorption diffusivity relaxes with time from D_i to $D_\infty(\varphi_{fin}) = D_\infty(\varphi_{eq}) = D_{eq}$, whereas in desorption it relaxes from D_{eq} to $D_\infty(\varphi_{fin}) = D_\infty(0) = D_i$. It must be observed that differential or incremental sorption could also be modeled by resorting to the proper initial and boundary conditions without changing the mathematical formulation.

In the present analysis attention is confined to the planar geometry represented in Figure 1 and subject to symmetric initial and boundary conditions, so that the whole problem is symmetric.

With reference to the test in Figure 1, where δ represents the sample semithickness, the system is modeled as a one-dimensional domain and equations are made dimensionless through the following definitions:

$$x^+ = x/\delta;\ t^+ = t\,D_i/\delta^2;\ \varphi^+ = \varphi/\varphi_{eq};\ J^+ = J\,\delta/D_i;$$

$$\tau^+ = \tau\,D_i/\delta^2;\ D_r^+ = D_r/D_i;\ D_f^+ = D_f/D_i$$

Accordingly, the final form of the system of equations is as follows:

$$\varphi_{eq}\frac{\partial\varphi^+}{\partial t^+} = -\partial J^+/\partial x^+ \tag{21}$$

$$J^+ = J_r^+ + J_f^+ \tag{22}$$

$$J_r^+ = -D_r^+\,\varphi_{eq}\frac{\partial\varphi^+}{\partial x^+} - \tau^+\,\partial J_r^+/\partial t^+ \tag{23}$$

$$J_f^+ = -D_f^+\,\varphi_{eq}\frac{\partial\varphi^+}{\partial x^+} \tag{24}$$

$$D_r^+ = D_\infty^+(\varphi^+) - D_{in}^+ \tag{25}$$

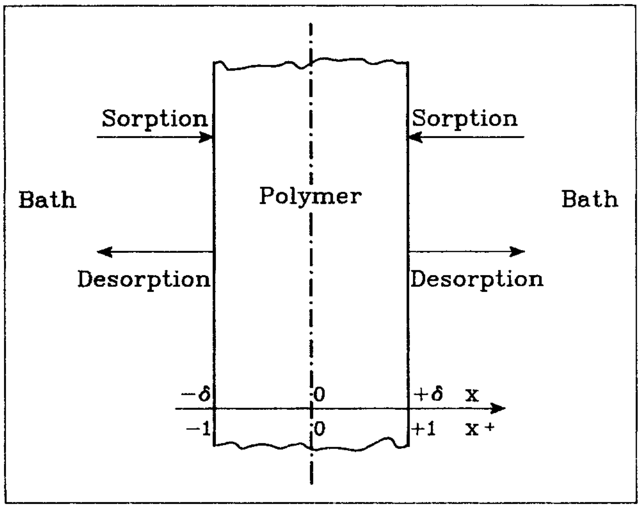

Figure 1. Sample test and coordinate system.

$$D_f^+ = D_{in}^+ \tag{26}$$

$$\tau^+(\varphi^+) = \{De\exp[K\varphi_{eq}(1-\varphi^+)]\}/R_d \tag{27}$$

$$D_\infty^+(\varphi^+) = R_d^{\varphi^+} \tag{28}$$

Initial conditions:

$$\varphi^+ = \varphi_{in}^+ \text{ for } -1 < x^+ < +1 \text{ and } t^+ = 0 \tag{29}$$

$$\varphi^+ = \varphi_w^+ \text{ for } x^+ = \pm 1 \text{ and } t^+ = 0 \tag{30}$$

$$J^+ = 0 \text{ for } -1 \le x^+ \le +1 \text{ and } t^+ = 0 \tag{31}$$

Boundary conditions:

$$\tau^+\,d\varphi^+/dt^+ = \varphi_{fin}^+ - \varphi^+ \text{ for } x^+ = \pm 1 \text{ and } t^+ > 0 \tag{32}$$

In the dimensionless problem the following quantities have been used:

$$R_d = D_{eq}/D_i;\ \varphi_{in}^+ = \varphi_{in}/\varphi_{eq}$$

$$\varphi_w^+ = \varphi_w/\varphi_{eq};\ \varphi_{fin}^+ = \varphi_{fin}/\varphi_{eq}$$

as well as the Deborah number $De = \tau_{eq}\,D_{eq}/\delta^2$.

According to the previously reported dimensional values for sorption and desorption cases, the values of φ_{in}^+, φ_w^+, φ_{fin}^+, and D_{in}^+ considered in the numerical calculations turn out to be:

Sorption

$$\varphi_{in}^+ = 0 \tag{33}$$

$$\varphi_w^+ = 0.8 \tag{34}$$

$$\varphi_{fin}^+ = 1 \tag{35}$$

$$D_{in}^+ = 1 \tag{36}$$

Desorption

$$\varphi_{in}^+ = 1 \tag{37}$$

$$\varphi_w^+ = 0.2 \tag{38}$$

$$\varphi_{fin}^+ = 0 \tag{39}$$

$$D_{in}^+ = R_d \tag{40}$$

Numerical Method

A numerical approach has been necessary to solve the governing system of eeuations. An analytical solution of the type shown by Adib and Neogi (1987) is not possible in the current formulation of the problem due to the nonlinearities arising from the functional dependence of τ and D_∞ on φ.

The ordinary differential equation that describes the penetrant solubility at the interface between the sample and the penetrant bath has been solved resorting to the simple integration method proposed by Gill (1951).

A finite-difference approach has been applied to the system of partial differential equations consisting of the mass balance together with the flux constitutive equation. So for these equations, discretization in the space coordinate has been performed by the control volume formulation, while the fully implicit method has been adopted to integrate the equations over a time step (for both the control volume formulation and the fully implicit method see Patankar, 1980).

The scheme has proved to effectively operate for any value of De ranging from 0 to ∞ in the current parabolic system of partial differential equations, whereas it cannot work for the limiting hyperbolic case already examined by Camera-Roda and Sarti (1986) resulting when $D_{eq}/D_{in} \rightarrow \infty$. In this latter case the numerical method by Lax and Wendroff (1960) was adopted to deal with the nonlinear formation of a concentration shock front.

In the space finite differences, linear variation of the values of the variables has been assumed, when necessary, between consecutive grid knots, and the grids for the diffusive flux and the penetrant volume fraction have been staggered as suggested by Patankar (1980) in order to improve accuracy. The nonlinear algebraic equations resulting from the discretization process have been cast into a linear form, leaving nonlinearities hindered in the values of the diffusivities $D_\infty(\varphi)$ and of the relaxation times $\tau(\varphi)$. In this way, after substitution of the flux expressions into the mass balance equations, a tridiagonal system of apparently linear equations holds where the unknowns turn out to be just the penetrant volume fractions at each grid knot. The Thomas algorithm has been adopted to directly solve the set of linearized equations. By repeatedly solving this linear system (updating at each iteration the values of $D_\infty(\varphi)$ and $\tau(\varphi)$ at every grid knot), convergence is reached very soon at each time step. Fluxes can be sequentially computed from the discretized expressions of the constitutive equation.

Runs for different values of the parameters were accomplished by dividing the thickness of half the symmetric sample from $x^+ = -1$ to $x^+ = 0$ with a uniformly spaced grid of 51 points, and assuming a time step $\Delta t^+ = 3.8 \times 10^{-4}$. Test runs showed that these values are sufficient to guarantee small discretization errors and stability.

Results

The main feature of the model is the capability of reproducing both Fickian and non-Fickian behavior according to the values of certain intervening parameters.

Clearly the parameters determining the different types of behavior are mainly the diffusive Deborah number De (Vrentas et al., 1975; Vrentas and Duda, 1977) together with the diffusivity ratio R_d. At very small Deborah numbers a Fickian transport is actually observed as relaxation happens almost instantaneously. Very large Deborah numbers again reproduce Fickian diffusion since relaxation is allowed to take place only at very long times when diffusion has already acted to reach equilibrium. In the latter case however a subsequent "relaxation" sorption is obtained due essentially to the change in the solubility at long times, as described by boundary condition Eq. 12. On the other hand, it is apparent that R_d is connected to the relative weight of the diffusivity D_r in the relaxing flux term to the Fickian diffusivity D_f, as, from the equations previously reported, it is $D_r/D_f = R_d^{\varphi^+}$ and $D_r/D_f = R_d^{\varphi^+} - 1$ for sorption and desorption, respectively. The effect is that Fickian transport is reproduced by $R_d = 1$, which implies a vanishing relaxation term, while deviations from Fickian behavior and anomalous diffusion are more significant the larger R_d is. Therefore, in the present work the effect of a variation of both these parameters is studied, all the remaining parameters being kept constant at $\varphi_{eq} = 0.2, K = 12$.

Since the manifestation of anomalous diffusion is mainly through effects such as nonlinear dependence of mass sorption on the square root of the time, the formation and propagation of a shock concentration front, and the possible overshoot of the mass uptake with respect to the final equilibrium value, then the existence of non-Fickian behaviors can be detected by plotting both the weight uptake vs. time and the concentration profiles.

Curves of the dimensionless mass uptake $M^+ = M/M_{eq}$ vs. $\sqrt{t^+}$ in a sorption process are reported in Figure 2 at different Deborah values for $R_d = 10$. The curve at $De = 0$ represents the case of an instantaneous relaxation and, as a consequence, clearly shows a typical Fickian behavior with linear variation of M^+ with $\sqrt{t^+}$ and no overshoot or oscillation. In fact $De = 0$ implies $\tau = 0$ and hence a constitutive equation for the flux given by

$$J^+ = -(D_r^+ + D_f^+)\, \varphi_{eq}\, \partial\varphi^+/\partial x^+ \tag{41}$$

or, by substitution of the expressions of D_r^+ and D_f^+,

$$J^+ = -D_\infty^+ (\varphi^+)\, \varphi_{eq}\, \partial\varphi^+/\partial x^+ \tag{42}$$

which formally yields a Fickian constitutive equation with nonconstant diffusivity.

The same sorption mechanism but with constant diffusivity is reproduced by the curve for $De = \infty$, as J_r^+ never relaxes and remains at the initial value $J_r^+ = 0$, so that the following Fickian constitutive equation holds:

$$J^+ = J_f^+ = -D_f^+ \varphi_{eq} \frac{\partial\varphi^+}{\partial x^+} = -D_{in}^+ \varphi_{eq} \frac{\partial\varphi^+}{\partial x^+} \tag{43}$$

Furthermore, Figure 2 shows that the sorption process is faster for $De = 0$ than for $De = \infty$ as was expected on the

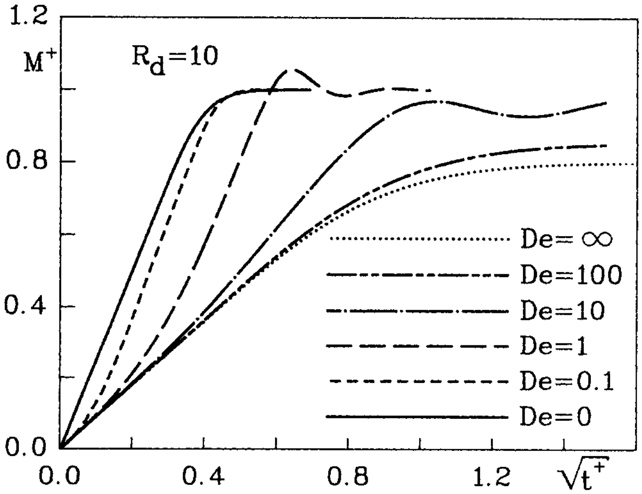

Figure 2. Sorption curves of M^+ vs. $\sqrt{t^+}$ for $R_d = 10$ at various Deborah numbers.

difference in the respective diffusivities D^+_∞ and D^+_{in}, their ratio being $D^+_\infty/D^+_{in} = R_d^{\varphi^+}$ during sorption. Moreover, a contribution to a higher diffusion rate for $De = 0$ is determined by the unity value instantaneously attained by φ^+ at the interface at $x^+ = \pm 1$ with respect to the lower value $\varphi^+ = \varphi^+_w = 0.8$ frozen at $x^+ = \pm 1$ when no relaxation occurs ($De = \infty$).

Only at intermediate values of *De* is non-Fickian transport expected with several different manifestations, such as anomalous diffusion, case II transport, overshoots, and even oscillations in the mass uptake. Indeed this pattern is exhibited in Figure 2 by the curves for $De = 1$ and $De = 10$, whereas the $De = 0.1$ and $De = 100$ curves already approach the extreme trends depicted for $De = 0$ and $De = \infty$, respectively.

Similar considerations can be drawn for the curves reported in Figure 3, where the same quantities as in Figure 2 are plotted for a diffusivity ratio $R_d = 100$. A larger R_d magnifies the effects with larger deviations from the Fickian behavior for the intermediate values of *De* ($De = 1$, 10, and 100) and larger differences of the sorption rates between the two limit cases of $De = 0$ and $De = \infty$ due to the larger differences in the respective diffusivities.

It is worth noticing that the sorption curve for $De = \infty$ is independent of R_d since, when no relaxation takes place, the constant initial diffusivity is always effective.

When the M^+ vs. $\sqrt{t^+}$ curves of Figure 3 are reported on logarithmic scales, Figure 4, an evaluation is easily obtained for the power of time the penetrant mass uptake is proportional to. The slope of the $De = 0$ and $De = \infty$ curves is 0.5, that is, M^+ is indeed of Fickian type. The slope of the other curves ranges between 0.5 and 0.98 according to the value of *De* considered. Furthermore, the same curves usually exhibit a slight curvature, which denotes an acceleration in the weight uptake. This latter phenomenon is mainly caused by the relaxation of the penetrant solubility at the interface, so that it is expected that the parameter φ^+_w, which in the present computations was not varied, is also important for assessing the behavior of the system.

It is worth pointing out that proportionality of the penetrant mass uptake to a power of time ranging between 0.5 and 1, acceleration of the mass uptake before equilibrium, and overshoots have been experimentally observed in penetrant sorption in polymers (Bagley and Long, 1955; Newns, 1956; Fujita, 1961; Crank and Park, 1968; Alfrey et al, 1966; Hopfenberg, 1970, 1978; Jacques et al., 1973, 1974; Vrentas et al., 1975; Nicolais et al., 1977; Berens and Hopfenberg, 1978; Thomas and Windle, 1981; Sarti et al., 1983, 1984; Durning and Russel, 1985).

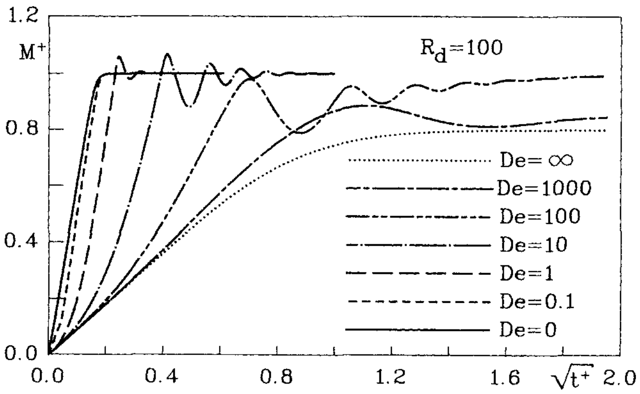

Figure 3. Sorption curves of M^+ vs. $\sqrt{t^+}$ for $R_d = 100$ at various Deborah numbers.

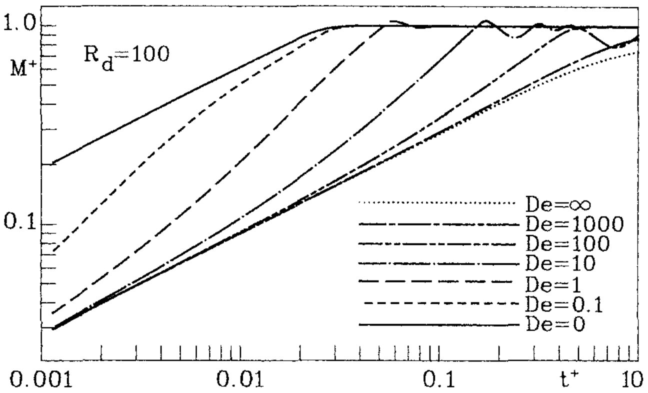

Figure 4. Log-log plot of sorption curves for $R_d = 100$ at various Deborah numbers.

Figure 5 allows a direct comparison of the mass sorption curves at different values of R_d in the case of $De = 1$, that is, for a Deborah number implying that relaxation happens on a time scale comparable with that of the diffusion process. A scrutiny of the curves confirms the previous observations on the increasing magnitude of the anomalous mass transport characteristics with increasing value of R_d. It is also apparent that the higher R_d, the larger the sorption rate; the reason for this dependence lies in the proportionality of the final diffusivity D_{eq} to R_d. The case of $R_d = D_{eq}/D_i = 1$ is characterized by a constant diffusivity, that is, the flux does not relax; therefore the curve for $R_d = 1$ refers to a Fickian transport, even if the relaxation of the penetrant

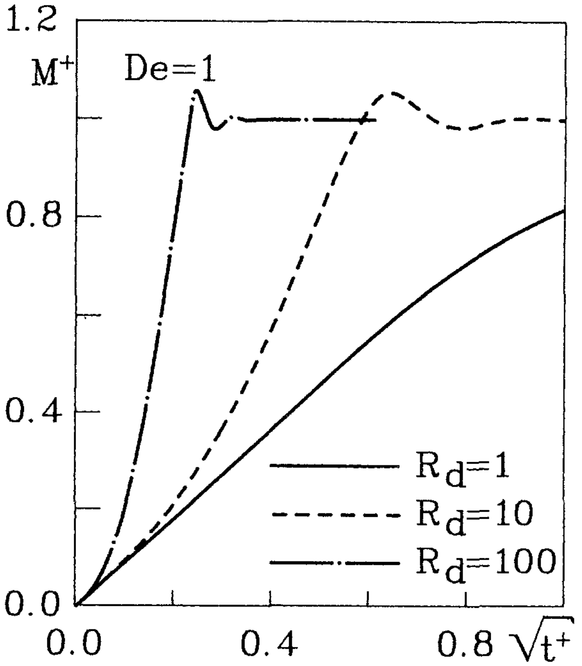

Figure 5. Sorption curves of M^+ vs. $\sqrt{t^+}$ for $De = 1$ at various values of R_d.

solubility, which takes place at the interface at $x^+ = \pm 1$, results in the presence of a flex point.

Penetrant concentration profiles are reported at various time levels in Figures 6–9 for different combinations of the parameters De and R_d.

In Figure 6 where a large value of R_d ($R_d = 100$) and an intermediate value of De ($De = 1$) are assumed, the non-Fickian nature of the transport process is evident. Relaxation takes place during the sorption process so that there exist zones where concentration changes are sufficiently slow to allow the flux to follow the variation of the driving force. Other zones experience changes of concentration too fast to allow for changes in the relaxing term of the flux even in presence of a steep concentration profile. The consequences are very similar to those obtained from hyperbolic problems: a concentration profile very similar to a shock front is formed and is detected by the onset of an outward concentration wave after the two penetrant fronts coming from the two boundaries of the sample have superimposed at the midplane at $x^+ = 0$. The latter phenomenon is responsible for the overshoots of M^+ with respect to the equilibrium value. On the other hand, successive reflections of the concentration wave, not shown in the figure for clarity, are responsible for the oscillations of M^+ also observed in the hyperbolic problem in Camera-Roda and Sarti (1986).

It is worth pointing out that in the cases reported above, if the model predicts case II transport, it formally predicts also an overshoot in the mass uptake in view of the hyperbolic behavior previously discussed. The latter effect, however, can be quantitatively so small as to be well below the experimental errors associated with the available data and can disappear in other cases still characterized by case II behavior for appropriate values of the parameters.

In Figure 7, where relaxation is instantaneous ($De = 0$), all hyperbolic characteristics disappear; concentration profiles show nothing similar to spatial discontinuity and are typical of Fickian diffusion with a highly concentration-dependent diffusivity. In fact, as already mentioned, the effective diffusivity is $D^+_\infty(\varphi^+) = R_d^{\varphi^+} = 100^{\varphi^+}$. In view of the assumed large value of R_d ($R_d = 100$), the diffusivity D^+_∞ varies from 1 when $\varphi^+ = 0$ to 100 when $\varphi^+ = 1$. This large variation causes the onset of a flex point in the concentration profile. This is not the case for the Fickian transport with constant diffusivity, reflected by the curves in Figure 8, where $De = \infty$ implies that the effective diffusivity remains at the initial value independent of φ^+ and R_d.

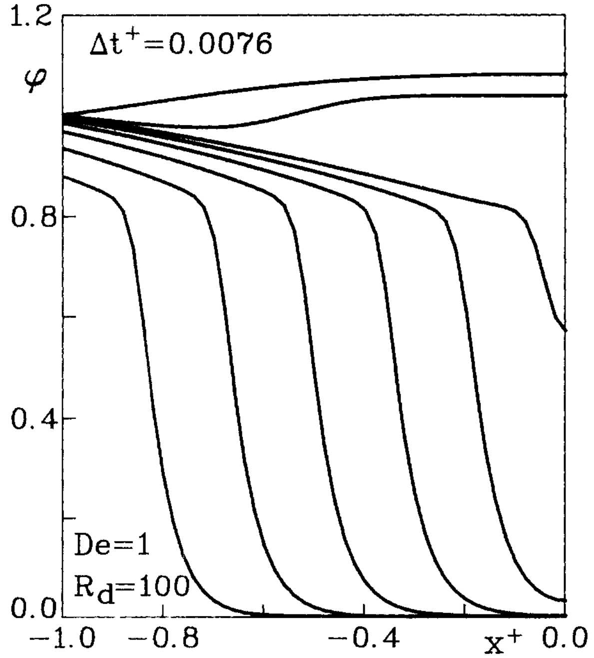

Figure 6. Concentration profiles during sorption at constant time intervals ($\Delta t^+ = 0.0076$) for $De = 1$ and $R_d = 100$.

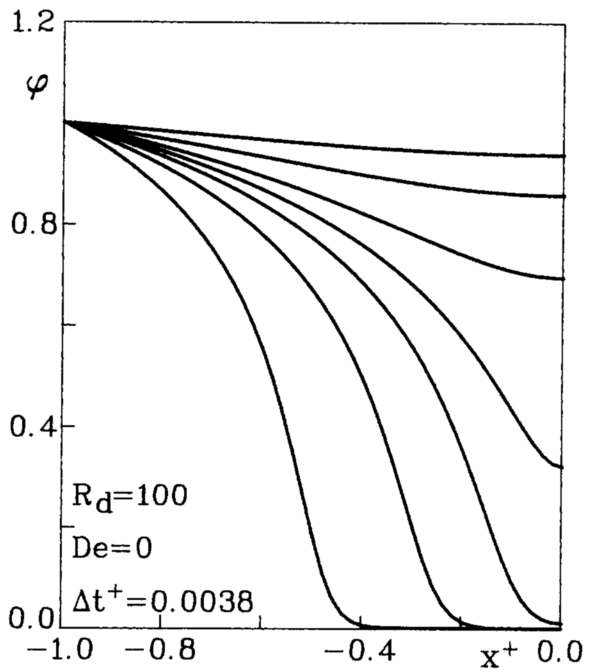

Figure 7. Concentration profiles during sorption at constant time intervals ($\Delta t^+ = 0.0038$) for $De = 0$ and $R_d = 100$.

The concentration profiles for $De = 1$ but a smaller value of R_d ($R_d = 10$) are reported in Figure 9. The flux has sufficient time to relax during the sorption process so that hyperbolic peculiarities are still shown, but are less evident than for $R_d = 100$, as the smaller R_d, the lower the importance of J^+_r on J^+.

The desorption process has also been investigated and the relevant penetrant mass content M^+ vs. $\sqrt{t^+}$ curves are reported in Figures 10 and 11 for some combinations of the parameters. It should be pointed out that contrary to sorption, the effective diffusivity is diminishing with time from $D^+_{eq} = D^+_\infty(1) = R_d$ to $D^+_\infty(0) = 1$, the dimensionless intrinsic diffusivity of the unpenetrated polymer.

The influence of a variation of De can be appreciated in Figure 10, where curves are plotted for three different values of De and a large value of R_d ($R_d = 100$) to magnify the effect of the relaxing flux term. Both the two borderline cases, $De = 0$ and $De = \infty$, reproduce Fickian transport but with different diffusivities. For $De = \infty$ no relaxation occurs so that diffusivity is frozen at the initial value $D^+_{eq} = R_d$, whereas for $De = 0$ the local effective diffusivity instantaneously attains the value $D^+_\infty(\varphi^+) = R_d^{\varphi^+}$ that ranges between 1 and R_d according to the local value of φ^+. The effect should be a higher dimensionless

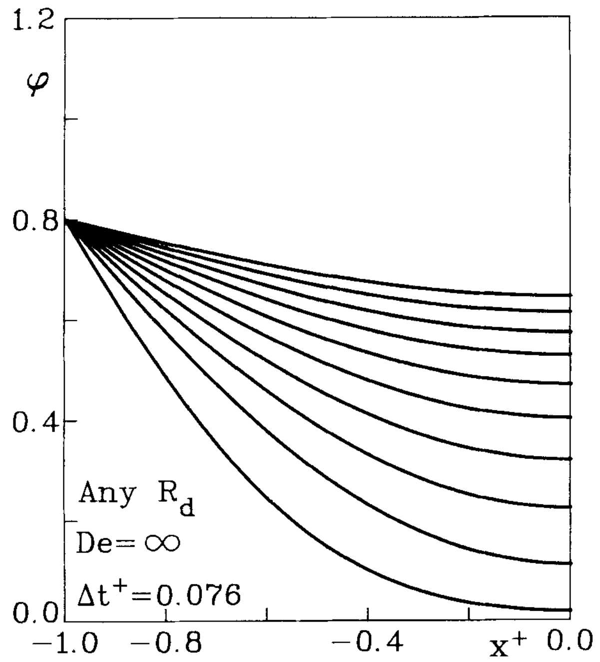

Figure 8. Concentration profiles during sorption at constant time intervals ($\Delta t^+ = 0.076$) for $De = \infty$.

mass desorption rate for $De = \infty$ than for $De = 0$. Actually, a variation of the Deborah number also determines differences in the rates of relaxation of the penetrant solubility at the bath-polymer interface, so that a cross of the M^+ curves after certain times is detected. The value $De = 0.1$ is representative of a case with a relaxation time scale of the same order of magnitude as the diffusion time scale. The consequence is that non-Fickian transport is effective and the relevant curve at early times lies between the $De = 0$ and the $De = \infty$ curves.

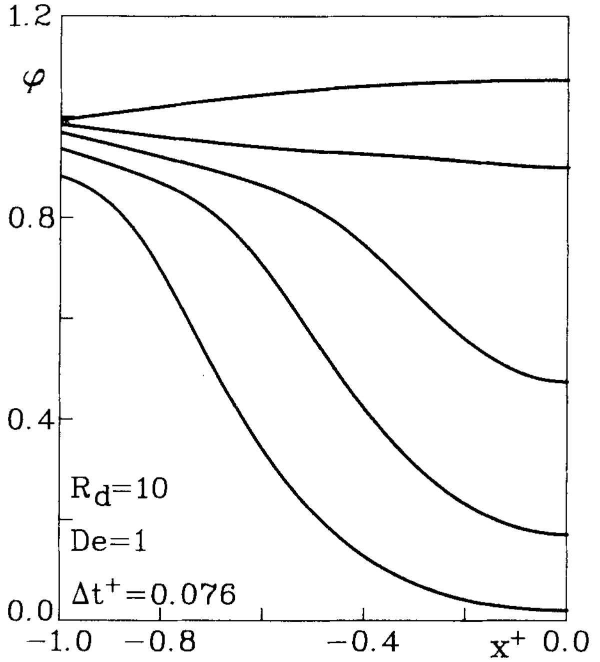

Figure 9. Concentration profiles during sorption at constant time intervals ($\Delta t^+ = 0.076$) for $De = 1$ and $R_d = 10$.

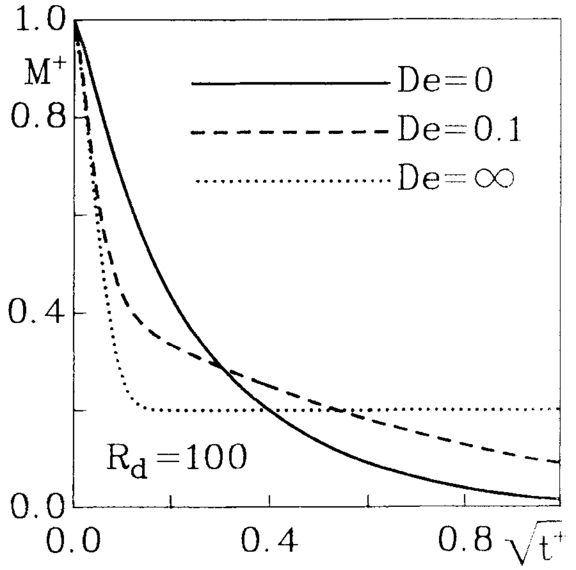

Figure 10. Desorption curves of M^+ vs. $\sqrt{t^+}$ for $R_d = 100$ at various Deborah numbers.

It is worth noticing that for given R_d and De the characteristic time of diffusion is faster for desorption than for sorption since the process starts with the highest value of diffusivity, which is the value pertaining to the completely relaxed polymer at $\varphi^+ = 1$.

The curves in Figure 11 show that for a given De (in the investigated case, $De = 1$) the mass desorption rate is higher as R_d is larger. The reason is that the initial diffusivity is proportional to R_d; only at longer times does diffusivity change toward the final unity value, with a rate that diminishes with De and is zero for $De = \infty$.

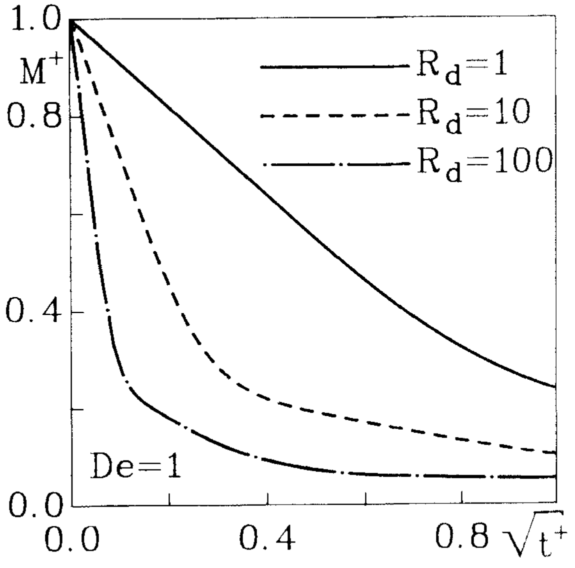

Figure 11. Desorption curves of M^+ vs. $\sqrt{t^+}$ for $De = 1$ at various values of R_d.

So the curve for $R_d = 1$ is for a constant diffusivity and appears to be almost linear with $\sqrt{t^+}$ during most of the time. A slight curvature of this curve is caused by the relaxation of the penetrant solubility at the $x^+ = \pm 1$ interface.

The $R_d = 100$ case does not significantly experience relaxation since desorption happens in shorter times than relaxation. On the contrary, for $R_d = 10$ the desorption times become sufficiently long, when $De = 1$, to let the flux relax to some extent. The result is that the corresponding curve is not linear with $\sqrt{t^+}$ except at the very beginning of desorption.

Conclusions

A model of penetrant diffusion in polymers has been presented that takes simultaneously into account diffusive flux constituted by a Fickian term plus a relaxing one, dependence of the physical quantities on concentration, and relaxation of the penetrant solubility at the bath-polymer interface. A physical meaning can be associated with the intervening parameters. Furthermore, the current model is not an *ad hoc* model. In fact, it can envisage both Fickian and non-Fickian transport and can deal equally well with integral or differential sorption and desorption processes with no modification of the mathematical formulation, just by resorting to the relevant initial and boundary conditions.

The model is based on the observation that a delay may hold between the changes in the concentration gradient and the response of the relaxing term of the flux due to stress and molecular rearrangements or morphological changes accompanying the penetrant transport inside the polymer matrix. If the retard is very short or very long with respect to the diffusion process then Fickian law is recovered, otherwise, anomalous behaviors arise. If the retard is rather long with respect to the diffusion time, a relaxation weight uptake can be shown even in the absence of concentration gradients, due to the changes in solubility. The parameter describing the time scale ratio of relaxation to diffusion is the Deborah number. On the other hand, the extent of the anomalities depends on the relative weight in the flux constitutive equation of the relaxing term to the nonrelaxing one that is described by the parameter R_d.

It is concluded that a combination of De and R_d determines the manifestation of non-Fickian mechanisms of mass transfer. The results obtained by numerically solving sorption and desorption problems indicate that the model appears to be potentially able to describe, albeit qualitatively, all the Fickian and non-Fickian behaviors observed experimentally.

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