Mathematical model of the desorption of swelling solvents from swollen polymer films

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Desorption of swelling solvents from swollen polymer samples presents several interesting features. Initial rates of desorption are often very significantly larger than absorption rates, while long term desorption rates are extremely slow. A mathematical model which has recently been applied successfully to the analysis of absorption phenomena is extended to desorption. The model predicts all the experimentally observed features of desorption, without need of adjustable parameters.

INTRODUCTION

The use of thin polymeric films in packaging is growing rapidly. In a variety of membrane applications a polymeric film may be employed for separations. Polymeric coatings are also used to resist corrosion and contamination. In all the applications not only are the rates of diffusion of various species through the polymeric film important but an even more significant problem arises when these films are made. This is the removal of residual solvents and monomers which may be present in the polymeric film. Therefore, it is not surprising that the diffusion of solvents in solid polymers has been a subject of numerous theoretical as well as experimental investigations in the last two decades.

Many anomalies or deviations from Fick's law of diffusion are observed, particularly below the glass transition temperature of the polymer and above the threshold concentrations of the solvent. In general this question of non-Fickian or anomalous diffusion can be, perhaps arbitrarily, subdivided into two subquestions. The first one concerns sorption of solvents into the glassy polymers, and the second one deals with desorption of solvents from swollen polymers. The most characteristic feature of the former is that the weight of solvent sorbed into the polymer varies with time raised to an exponent between 0.5 and 1.0; the extreme case (1.0) being called Case-II transport. Most of the published literature are analyses of this phenomenon. Almost all of the analyses published up to 1976 assume a strong dependency of solvent diffusivity on concentration, though others based on swelling stresses, relaxation of polymer segments and convective flux of the solvent can also be found.[1-5] However, these models have had only limited success in interpreting experimental data on sorption.

The characteristic feature of the second part of the problem of anomalous diffusion is the observation of higher rates of desorption when compared to those of sorption over the same concentration interval.[6-8] This observation is an interesting contradiction of a well-known result in diffusion theory – for any diffusivity which is a monotonically increasing function of concentration of the diffusing species, the rate of desorption should always be smaller than or at most equal to that of absorption over the same concentration interval.[9] It is also surprising that, although a number of analyses have been made of the problem of sorption of solvents, practically none of the models presented so far have been aimed at explaining this intriguing feature of desorption of solvents from swollen polymers.

Recently, Astarita and Sarti[10] proposed a model which takes glassy to swollen transition kinetics explicitly into account. The model, later extended by Astarita and Joshi,[11] has been found to correlate and predict the data on absorption of solvents very well. Although the model does not rely upon the dependence of diffusivity on concentration, and in fact is based on the very crude hypothesis of constant diffusivity, it seems potentially capable of explaining the anomaly of higher desorption rates.

MODELING THE PHENOMENON

All the available data on desorption of solvents from swollen polymers appear similar, at least qualitatively; *Figure 1* is a typical sketch of such data. A small time asymptote is exhibited, where rates of desorption are large and proportional to the square root of time. A semi-infinite homogeneous polymer sample would never deviate from this asymptote if diffusivity is independent of concentration. As the data are taken on finite, polymer films, the deviation from the small time asymptote is unsurprising. However, what is significant is the rapid decrease in the rate of desorption and the extremely long tail of the desorption curve. In fact usually all of the solvent which goes into the polymer during sorption cannot be desorbed: a small amount always remains in the polymer, desorbing at very slow rates, typically this amount is only a few percents higher than the threshold concentration of the solvent required to swell the polymer.

Consider a flat slab of swollen polymer with uniform solvent concentration c_o which needs to be either greater

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than or equal to c^*, the threshold swelling concentration of the solvent. Both of these cases will be considered separately. The equilibrium concentration on the solvent-polymer interface will be assumed to be zero, though a case of non-zero, constant solvent-concentration at the interface can easily be treated along identical lines.

The diffusivities in the glassy and swollen regions will be assumed constant, though different from each other. The densities of both phases will be assumed to be equal to each other; in other words, the bulk movement of one phase with respect to the other will be neglected. When external solvent fugacity is decreased from f_o to zero, a film of glassy polymer will form on the surface. As the diffusivities are known to be very small through glassy polymer, the high initial rates of desorption can only occur if the thickness of the glassy film formed on the surface is extremely small.

When the advancement of the glassification front is viewed as a rate process and its kinetics are taken explicitly into account, the identification of the driving force is crucial. In the analysis of Astarita and Sarti, it was assumed that the driving force for swelling is the difference between the concentration of solvent at the front on the swollen side and the critical swelling concentration c^*. In addition a power law type of dependence of the rate of advancement of the front on this driving force was presumed. In this analysis glassification rather than swelling is dealt with; therefore, assuming that $\bar{c}^*$ is the concentration on the glassy side in equilibrium with the threshold swelling concentration c^* on the swollen side, the difference between the equilibrium solvent concentration $\bar{c}^*$ and the local solvent concentration at the glassification front should serve as the driving force. An identical power law type dependence following Astarita and Sarti is assumed with presumably identical values for the constants involved, ie,

$$\frac{d\Lambda}{dt} = K(\bar{c}^* - \bar{c})^n \qquad (1)$$

where $d\Lambda/dt$ denotes the rate of advance of the glassification front. Careful analysis also reveals that the driving force should be located on the glassy side of the front, and the concentration on the swollen side of the front should be equal to the critical swelling concentration c^*. The analysis proceeds along identical lines to the analogy presented by Astarita and Sarti.[10]

The moving boundary Stefan problem can now be formulated as follows:

For the glassy film:

$$\bar{D}\,\frac{\partial^2 \bar{c}}{\partial x^2} = \frac{\partial \bar{c}}{\partial t} \qquad 0 \leqslant x \leqslant \Delta(t) \qquad (2)$$

with boundary condition

$$\bar{c}(0,t) = 0 \qquad (3)$$

For the swollen part:

$$D\,\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \qquad \Lambda(t) \leqslant x \leqslant \chi \qquad (4)$$

with boundary conditions

$$c(\Lambda(t),t) = c^* \qquad (5)$$

$c(\infty,t)$ bounded or $\partial c/\partial x(x,t) = 0$ for semi-infinite and finite films, respectively, and the initial conditions

$$c(x,0) = c_o \qquad (6)$$

$$\Lambda(0) = 0 \qquad (7)$$

The rate of advance of the front is given by:

$$\frac{\mathrm{d}\Lambda}{\mathrm{d}t} = K(\bar{c}^* - \bar{c})^n \qquad (8)$$

and the material balance across the front is written as

$$\bar{D}\,\frac{\partial \bar{c}}{\partial x} + \frac{\mathrm{d}\Lambda}{\mathrm{d}t}(\bar{c} - c^*) = D\,\frac{\partial c}{\partial x} \text{ with } x = \Lambda(t) \qquad (9)$$

The experimental observation of large initial rates of desorption implies that Λ is very small, and therefore $\mathrm{d}\Lambda/\mathrm{d}t$ is also very small. Equation 8 therefore suggests that the following assumption is justified:

$$\bar{c}(\Lambda,t) = \bar{c}^* \qquad (10)$$

Of course, equation 10 cannot be exact at $t = 0$, since from equations 3, 7 and 8 we get

$$\left.\frac{\mathrm{d}\Lambda}{\mathrm{d}t}\right|_{t=0} = K(\bar{c}^*)^n \qquad (11)$$

However, the initial finite rate of advance given by equation 11 may rapidly quench itself, and after a 'quenching time' t_c the approximation in equation 10 should be correct. The model equations will be developed on the basis of equation 10, before estimating the quenching time t_c: it will be seen that t_c is at most 10^{-4} s.

Semi-infinite slab, $c_o > c^*$

With the approximation of equation 10, the moving boundary problem for a semi-infinite slab is easily solved by a change of variables such as introduced by Neumann:[12]

$$\xi = x/t^{1/2} \qquad (12)$$

$$\bar{\xi} = \Lambda(t)/t^{1/2} \qquad (13)$$

The partial differential equations (2), (4) and (9) become ordinary ones, and by straightforward integration one obtains:

$$\bar{c}^* = (\pi\bar{D})^{1/2}\bar{\beta}\,\mathrm{erf}\,\bar{\xi}/2\,\bar{D}^{1/2} \qquad (14)$$

where $\bar{\beta}$ is an as yet undetermined constant.
Equation 14 implies that $\bar{\xi}$ is a constant, ie, from equation 13:

$$\Lambda = \bar{\xi}\,t^{1/2} \qquad (15)$$

Again from straightforward integration one obtains:

$$c_o - \bar{c}^* = \beta(\pi D)^{1/2}\,\mathrm{erfc}\,\bar{\xi}/2D^{1/2} \qquad (16)$$

$$\bar{D}\bar{\beta}\exp\frac{-\bar{\xi}^2}{4\bar{D}} + \frac{(\bar{c}^* - c^*)\bar{\xi}}{2} = D\beta\exp\frac{-\bar{\xi}^2}{4D} \qquad (17)$$

Equations 14, 16 and 17 can be solved to yield the values of the three constants β, $\bar{\beta}$ and $\bar{\xi}$; in particular the following equation is obtained for $\bar{\xi}$:

$$\left(\frac{\bar{D}}{\pi}\right)^{1/2}\frac{\bar{c}^*}{\mathrm{erf}(\bar{\xi}/2\bar{D}^{1/2})}\exp\frac{-\bar{\xi}^2}{4\bar{D}} + \frac{\bar{c}^* - c^*}{2}\,\bar{\xi}$$

$$= \left(\frac{\bar{D}}{\pi}\right)^{1/2} \frac{c_o - c^*}{\mathrm{erfc}\,(\bar{\xi}/2D^{1/2})} \exp\frac{-\bar{\xi}^2}{4D} \tag{18}$$

The solution is considerably simplified because $\bar{D} \ll D$, which (as will be seen below) implies that

$$\bar{\xi} \ll \bar{D}^{1/2} \tag{19}$$

so that equation 18 reduces to:

$$\bar{\xi} = (\pi\bar{D})^{1/2} \left(\frac{\bar{D}}{D}\right)^{1/2} \frac{\bar{c}^*}{c_o - c^*} \tag{20}$$

Considerations of equations 15 and 20 shows that the glassy film thickness Λ is very small indeed.

Finally, the rate of desorption is calculated as:

$$\frac{\mathrm{d}W}{\mathrm{d}t} = -(c_o - c^*)\left(\frac{D}{4t}\right)^{1/2} \tag{21}$$

Equation 21 shows that the model considered here predicts the initial high rates of desorption, and the fact that W is linear in $t^{1/2}$.

The quenching time t_c can now be estimated. The largest possible value of $\mathrm{d}\Lambda/\mathrm{d}t$ is given by equation 11; equation 15 would predict $\mathrm{d}\Lambda/\mathrm{d}t \to \infty$ as $t \to 0$. An estimate of t_c is obtained by requiring $\mathrm{d}\Lambda/\mathrm{d}t$ as given by equation 15 to have the value in equation 11; this yields:

$$t_c^{1/2} = \frac{\bar{D}}{k(\bar{c}^*)^n}\left(\frac{\pi}{D}\right)^{1/2} \frac{\bar{c}^*}{c_o - c^*} \tag{22}$$

Realistic values for the parameters appearing on the RHS of equation 22 are available;[11] from these, it may be calculated that t_c is of the order of 10^{-4} s at the most. Therefore, desorption during the quenching time may be neglected altogether.

Although the results in this section are for a semi-infinite slab, they are useful to describe the short-term behaviour of finite-thickness samples. Three points need to be stressed. The first is that, according to equations 15 and 20, the thickness of the glassy film is so small that it can be neglected altogether. The only effect that the formation of the glassy film has is to reduce the driving force for desorption from c_o to $c_o - c^*$; see equation 21. Indeed, whenever $c^* \ll c_o$, desorption from the swollen core takes place initially at essentially the same rate as if there were no glassy film at all.

The second point is that, based on equation 21, values of the diffusivity in the swollen phase can be extracted from initial rates. *Table 1* reports values of D calculated in this way from the data of Watt[13] for desorption of various solvents from wool Keratin.

The third point to be stressed is that, since $\mathrm{d}\Lambda/\mathrm{d}t$ is so small, one would need to go to inordinate lengths of time in order to glassify a non-negligible fraction of the sample; this in turn implies that for all practical purposes desorption will cease once the concentration has dropped to c^* throughout the swollen core. This prediction of the model is in good agreement with the observed behaviour.

Finite-thickness sample, $c_o > c^*$

The finite thickness model equations do not have a closed form analytical solution. However, the results in the preceding section show that, as long as the concentration in the swollen core is not almost equal to c^*, the presence of a glassy film manifests itself only by lowering the driving force from c_o to $c_o - c^*$. With such an approximation, the problem reduces to the familiar one which has the well-known solution:

Table 1 Values of D for Wool Keratin at 35°C*

Sorbate	$\bar{D}$ (cm^2/sec)	D (cm^2/sec)
Methanol	4.5×10^{-12}	1.1×10^{-7}
Formic acid	5.3×10^{-13}	3.3×10^{-8}
Ethanol	5.0×10^{-13}	6.8×10^{-9}
n-propanol	5.0×10^{-14}	2.7×10^{-8}
Acetic acid	2.5×10^{-11}	4.3×10^{-9}

*Values of $\bar{D}$ are as reported by Watt[13]

$$\frac{c - c^*}{c_o - c^*} = 2\sum_0^\infty \frac{(-1)^n}{(n + 1/2)^\pi} \exp\left[\frac{-(n + 1/2)\pi^2 Dt}{\chi^2}\right] \times \cos\left[(n + 1/2)\frac{\pi x}{\chi}\right] \tag{23}$$

Comparison of the predictions of equation 23 with experimental data is unfortunately difficult because desorption data are available for systems for which the value of c^* is not well established. However, if c^* is assumed to be equal to the (apparent) asymptotic value of the residual concentration in the sample, equation 23 correlates well the desorption rate data, indicating that the dependency of diffusivity on concentration, if not zero, is in fact of minor importance.

However, the real test of our model is based on the fact that it predicts the existence of an extremely thin glassy layer up to the end of region II in *Figure 1*. Therefore, the model predicts that, if a sample from which desorption has taken place to that limit is exposed again to a high external activity of solvent, it will absorb at a much faster rate than in the first cycle, since there would now be no glassy → swollen kinetic resistance. Furthermore, the model predicts that such a reabsorption process would proceed as a classical Fickian process.

Both predictions are well confirmed by available experimental data. Pogany[14] reports rates of water reabsorption into polystyrene at 80°C twice as large as the rates of initial absorption at 100°C. Baird, Hopfenberg and Stannett[15] report rates of reabsorption which are at least four times larger than the rates of initial absorption of *n*-pentane in annealed polystyrene. Lewis[16] reports data for acetone in nitrocellulose; the initial rates of reabsorption are approximately equal to those of desorption, but about four times faster than rates of initial absorption; reabsorption appears to be Fickian.

This appears to be substantial evidence for the interpretation of region II in *Figure 1* on the basis of equation 23, with an appropriate value for c^*. The behaviour in region III (the 'very long time' region) is examined in the next section.

Finite thickness sample, $c_o = c^*$

For this case, the mathematical formulation is only marginally different from that for a slab with $c_o > c^*$. No diffusion takes place inside the swollen core, and therefore the finite-thickness and semi-infinite slab solutions coincide as

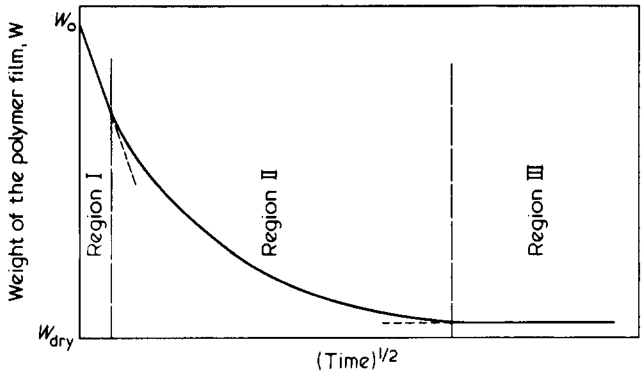

Figure 1 Weight of the polymer film *vs.* (time)$^{1/2}$

long as $\Lambda \leqslant \chi$. Only equations 2, 3, 7, 9 and 10 need to be considered; the RHS of equation 9 is equal to zero. Again a classical Neumann change of variables reduces the differential equations to ordinary ones, and by straightforward integration one obtains:

$$\frac{\mathrm{d}W}{\mathrm{d}t} = -\frac{\beta}{4}\left(\frac{\pi \bar{D}}{t}\right)^{1/2} \qquad (24)$$

where the constant β is to be calculated by solving simultaneously for β and γ the following two equations:

$$\beta e^{-\gamma^2} = 2(c^* - \bar{c}^*)\gamma \qquad (25)$$

$$\bar{c}^* = \beta \frac{\pi^{1/2}}{2} \operatorname{erf}\gamma \qquad (26)$$

An estimate of the magnitude of β can be obtained by considering the likely case where:

$$\frac{\bar{c}^*}{c^* - \bar{c}^*} \leqslant 1 \qquad (27)$$

If equation 27 is satisfied,

$$\beta = [2\bar{c}^*(c^* - \bar{c}^*)]^{1/2} \qquad (28)$$

With β evaluated from equation 28, comparison of equations 23 and 24 shows that the 'very long time' rate of desorption is indeed much smaller than the 'intermediate' one as long as the concentration in the swollen core is even very marginally larger than c^*.

CONCLUSIONS

A straightforward extension of the Astarita and Sarti model to the desorption case predicts qualitatively the desorption behaviour observed experimentally, for all three of the regions in *Figure 1.*

In particular, the fact that initial rates of desorption are often higher than rates of absorption is predicted. Indeed, whenever absorption rates are non-Fickian, the model predicts them to be significantly lower than Fickian. The same model, on the contrary, predicts desorption rates to be only marginally lower than calculated from classical Fickian theory.

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