Absorption–Desorption Histories Through a Sphere with a Change in Dimensions, with Constant Concentration on Surface During Absorption, and Finite Volume of Surrounding During Desorption

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SYNOPSIS

Liquids are transferred through nonporous polymers provoking a change in dimension. A mathematical treatment of the process of radial diffusion through a sphere with consequent change in dimension is made, as well as a numerical treatment of the process. The case is considered when the concentration of the liquid on the surface is constant during absorption and then the surrounding fluid is of finite volume and strongly stirred during the stage of desorption. The kinetics of absorption–desorption histories are calculated for various values of the volume expansion due to the presence of liquid. The profiles of concentration as well as the kinetics of change in dimension are also evaluated. Two parameters are introduced: the maximum of the volume expansion of the polymer and the ratio between the amount of liquid in the polymer and that contained in the surrounding at the final equilibrium of desorption. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

When a polymer is in contact with a diffusing substance, for example, a liquid, a mass transfer generally takes place and is controlled by diffusion. When this polymer is then being immerged into a surrounding atmosphere, a desorption of the substance can be observed. When the amount of transferred liquid is negligible, the process of diffusion can be described by Fick's laws established with constant dimensions of the solid.[1] It is well known that depending on the amount of the transferred diffusing substance, a change in dimensions of the solid is observed, especially with nonporous polymers such as rubbers or other elastomeric materials for which the amount of the transferred liquid can reach up to 100% of the volume of the solid or more.[2,3]

From a theoretical point of view, the mathematical treatment of diffusion through a solid with con-sequent change in dimension is of great interest. The classical studies leading to the second Fick's law, require constant dimensions of the solid whatever the amount of liquid transferred.[1] When a noticeable change in the dimensions of the solid is observed, the second Fick's law is thus not valid. From a practical point of view, the change in the polymer dimensions following the process of diffusion through this polymer may appear of high concern, especially in mechanics[2–4] or in other applications.

Applications of the swelling of biocompatible polymers in oral dosage forms for controlling the release of a drug in the stomach were considered,[5,6] and two dimensionless numbers were introduced with the Deborah and the Swelling interface numbers. In depth studies made on the interdiffusion of two diffusing substances provoking a volume change on mixing were summed up.[1] The kinetics of the swelling of acrylamide gels was determined by considering the shear modulus of the solid.[7] Even a far more complex system with various solvents and interpenetrating polymer networks was investigated, with the kinetics of swelling and equilibrium conditions showing that the number of phases in the
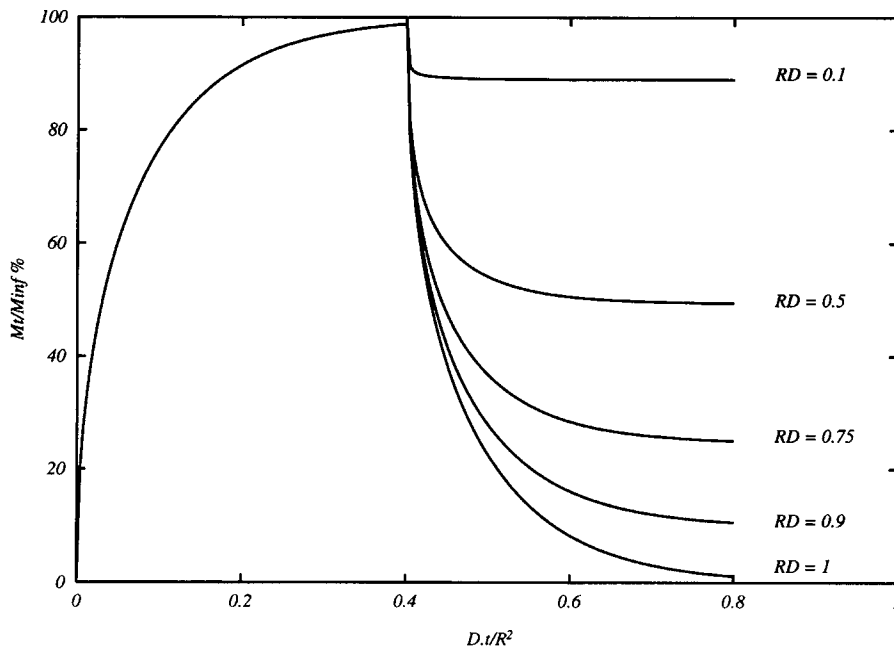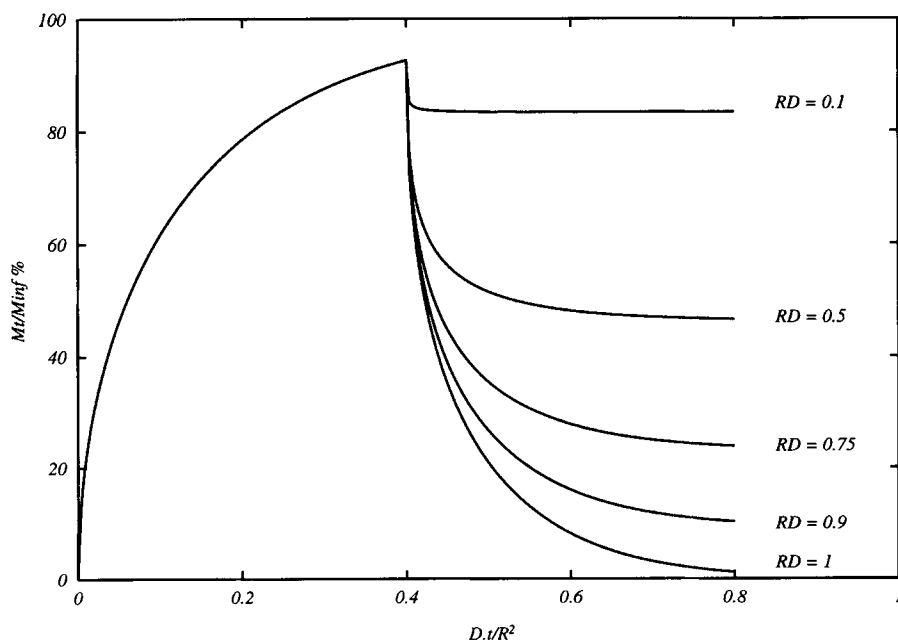
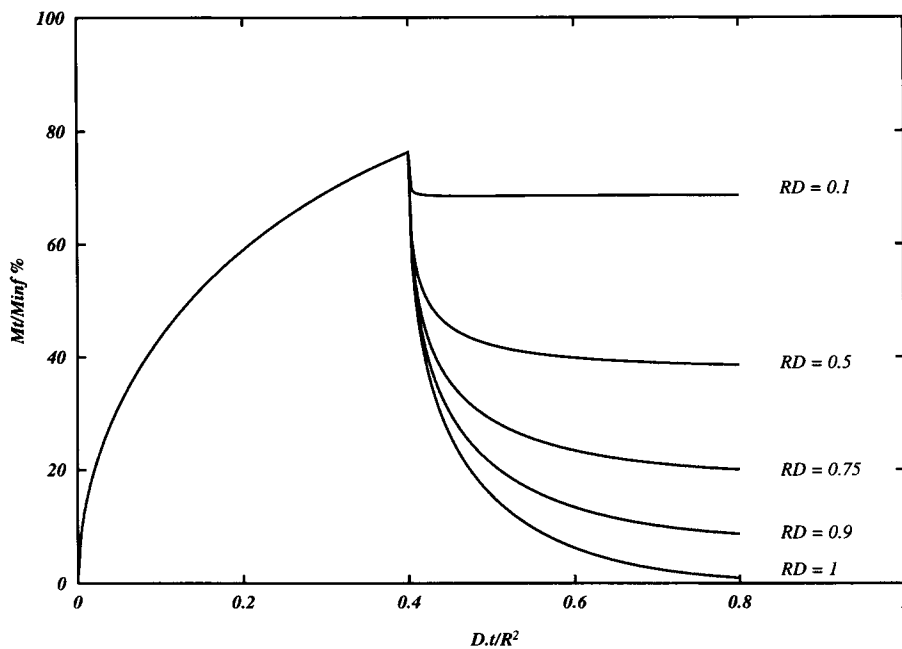**Figure 1**   Kinetics of absorption–desorption for various values of RD and for the value MRVE = 1.001.

system plays a major role.[8] The process of diffusion–evaporation of various substances with copolymers of ethylene vinyl acetate was studied by taking into account the consequent shrinkage, and a numerical model was established by Bouzon.[9,12,13] As a matter of fact, as already stated,[10] few studies have taken into consideration the kinetics of change in dimen-

sion associated with the diffusion of a liquid through a polymer.

The first objective in this article is to consider the case of absorption–desorption of a liquid associated with a consequent change in dimensions. The two stages of the process are controlled by radial diffusion through a polymer that is spherical in

Figure 2   Kinetics of absorption–desorption for various values of RD and for the value MRVE = 1.25.
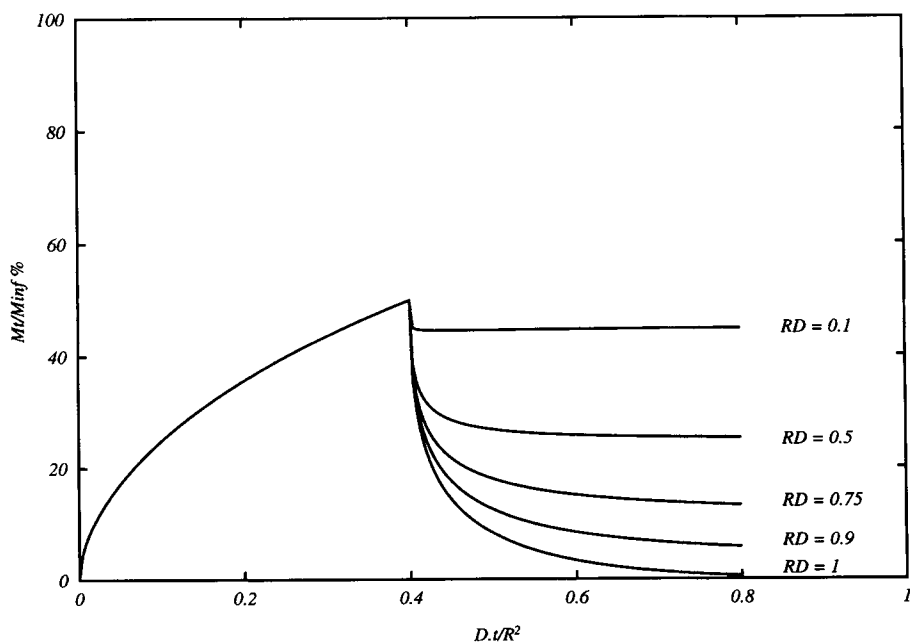
**Figure 3**   Kinetics of absorption–desorption for various values of RD and for the value MRVE = 2.5.

shape. As the coefficient of mass transfer on the surface of the polymer is very high, the concentration of the diffusing liquid on the surface is, at each moment, equal to the concentration required in the bead to maintain equilibrium with the external concentration existing at this precise moment. The following case is considered in particular: during the

stage of absorption, the polymer is in contact with the diffusing liquid, while during the stage of desorption, the polymer is in contact with a finite volume of a surrounding fluid that does not penetrate the polymer.

The other purpose of this study was to precisely determine the effect of the various parameters that

Figure 4   Kinetics of absorption–desorption for various values of RD and for the value MRVE = 5.0.
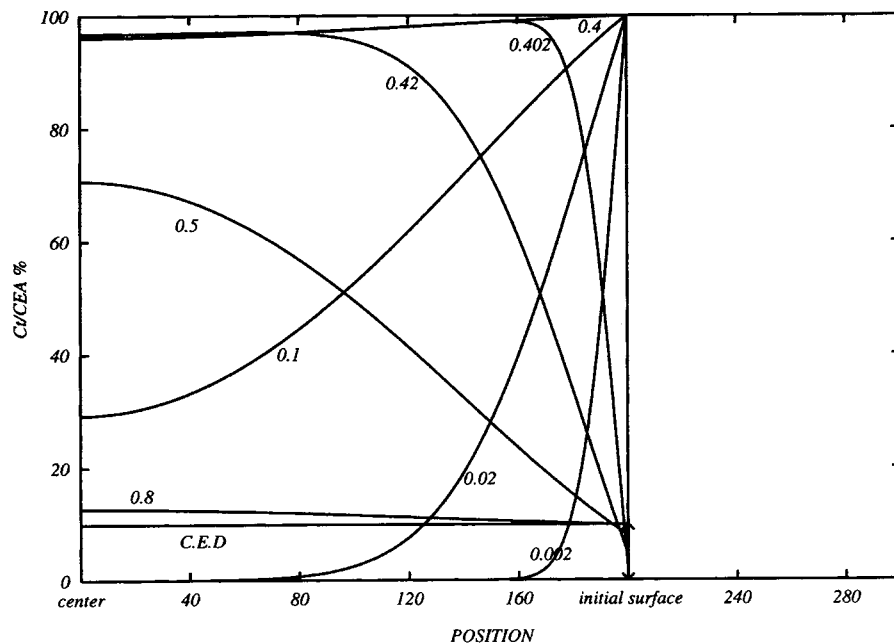
Figure 5   Concentration profile for various values of time t^*, for MRVE = 1.001, RD = 0.9, CED = 9.89.

intervene in the process: the relative volume expansion of the solid resulting from the presence of the liquid and the maximum value of this relative volume expansion; the ratio of the volumes of the polymer and the surrounding atmosphere during the stage of desorption; and the diffusivity of the substance through the polymer. A numerical model taking all the facts into account is derived and used for calculation.

THEORETICAL

Assumptions

The following assumptions are set forth in order to establish the problem clearly:

1. The polymer is spherical in shape and homogeneous, with a radial diffusion.
2. The volume of the bead is constantly equal to the sum of the volumes of the polymer and of the liquid located in it.
3. The coefficient of mass transfer on the surface of the polymer is so high that it may be considered as infinite, so that the internal concentration of the diffusing liquid at the surface of the bead is constantly in equilibrium with the external concentration that exists at the same time.
4. The stage of absorption is obtained by im-

mersing the solid in the pure liquid, so that the external concentration is uniform and constant, equal to the density of the liquid. Thus the liquid concentration on the surface reaches the value at equilibrium as soon as the process starts.

5. The surrounding fluid has a finite volume and is strongly stirred during the stage of desorption, so that the external concentration is constantly uniform and increases with time.
6. The internal pressure in the polymer due to its dilatation is not considered, although it may intervene, especially at the beginning of the stage of desorption.

Mathematical Treatment

Two kinds of abscissa are considered for characterizing the position of a point in the polymer: the canonical radial abscissa, u, that is to say the radial abscissa when the bead is liquid free; and the actual radial abscissa at time t, $r(u, t)$, that varies with the swelling. Of course, for $t = 0$:

$$r(u, 0) = u \quad \text{with} \quad 0 \le u \le R \qquad (1)$$

where R is the canonical radius of the bead, that is, its radius when it is free from liquid. The actual radius at time t is $r(R, t)$.

The membrane with a canonical average radius, u, and a canonical thickness, Δu, is considered. The
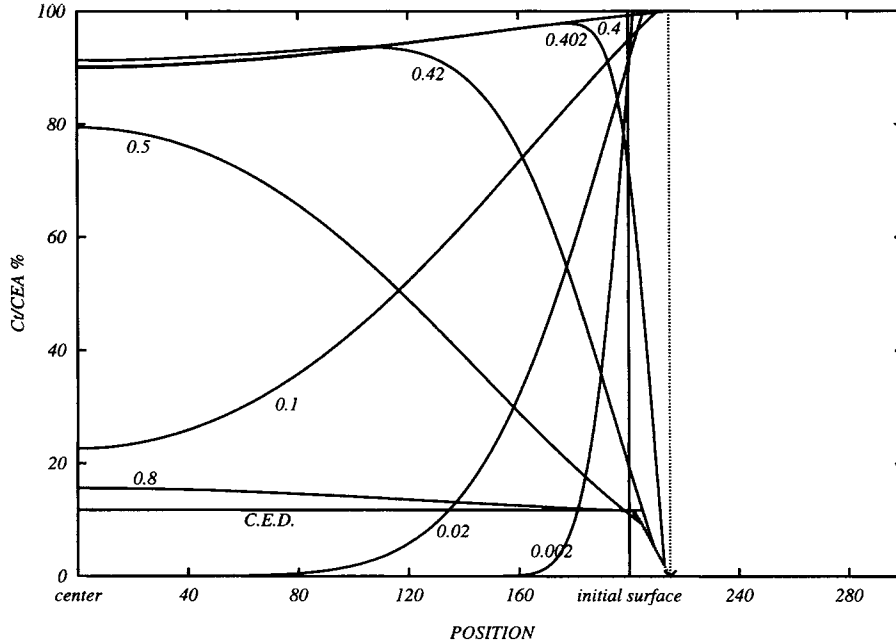
Figure 6 Concentration profile for various values of time t^*, for MRVE $= 1.25$, RD $= 0.9$, CED $= 11.75$.

volume of this membrane at time t, with some liquid in it, is:

$$V(u, t) = \frac{4\pi}{3}\left[r^3\left(u + \frac{\Delta u}{2}, t\right) - r^3\left(u - \frac{\Delta u}{2}, t\right)\right]$$

$$= \frac{4\pi}{3}\Delta(r^3). \quad (2)$$

The volume of the membrane free from liquid is:

$$V(u, 0) = \frac{4\pi}{3}\Delta(u^3). \quad (3)$$

The additivity of the volumes of polymer and liquid is written as follows:

$$V(u, t) = V(u, 0) + \frac{V(u, t) \cdot C(u, t)}{d} \quad (4)$$

where $C(u, t)$ is the average concentration of liquid in the membrane at time t, and d is the density of the liquid. $C(u, t)$ and d are expressed in the same units (g/cm^3).

The volume expansion is easily drawn from the above equations:

$$\frac{V(u, t)}{V(u, 0)} = \frac{\Delta(r^3)}{\Delta(u^3)} = \left[1 - \frac{C(u, t)}{d}\right]^{-1} \quad (5)$$

leading to the radial expansion:

$$\frac{\partial r}{\partial u} = \frac{u^2}{r^2} \cdot \left[1 - \frac{C(u, t)}{d}\right]^{-1}. \quad (6)$$

The mass balance during the interval of time $[t, t + \Delta t]$, within the membrane, when $\Delta t \rightarrow 0$, leads to:

$$\frac{\partial}{\partial t}[V(u, t) \cdot C(u, t)] = \frac{\partial}{\partial u}\left[A \cdot D \cdot \frac{\partial C}{\partial r}\right] \cdot \Delta u. \quad (7)$$

With the volume of this thin membrane drawn from eqs. (5) and (3), and when $\Delta u \rightarrow 0$, eq. (7) is rewritten as follows:
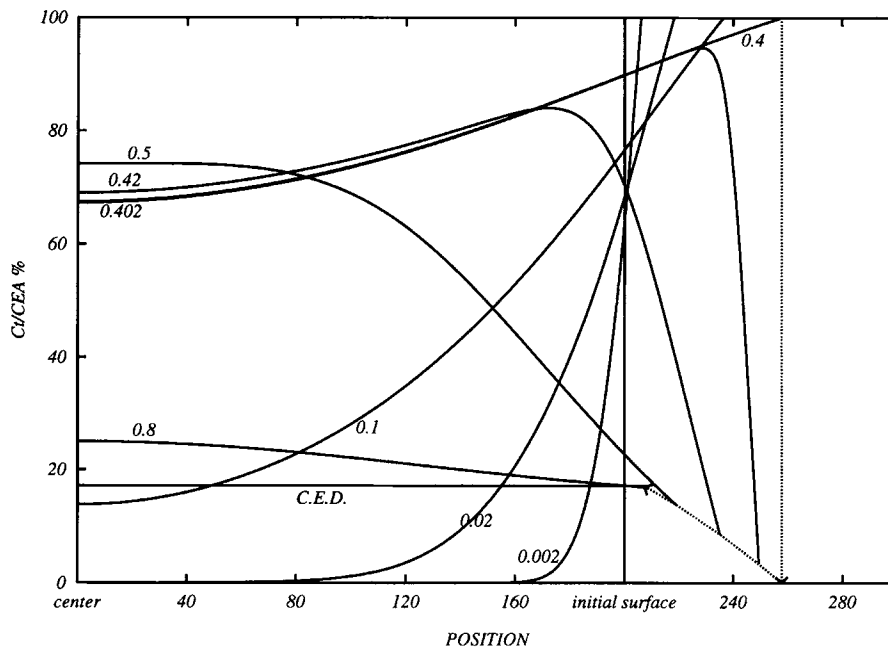
$$\frac{\partial}{\partial t}\left[\left(1 - \frac{C}{d}\right)^{-1} \cdot C\right] = \frac{1}{u^2} \cdot \frac{\partial}{\partial u}\left[r^2 \cdot D \cdot \frac{\partial C}{\partial r}\right]. \quad (8)$$

The gradient $\partial C/\partial r$ by using eq. (6) is:

$$\frac{\partial C}{\partial r} = \frac{\partial C}{\partial u} \cdot \frac{\partial u}{\partial r} = \frac{r^2}{u^2}\left[1 - \frac{C}{d}\right] \cdot \frac{\partial C}{\partial u} \quad (9)$$

and eq. (8) finally becomes:

$$\frac{\partial}{\partial t}\left[\left(1 - \frac{C}{d}\right)^{-1} \cdot C\right]$$

$$= \frac{1}{u^2} \cdot \frac{\partial}{\partial u}\left[\frac{r^4}{u^2} \cdot D \cdot \left(1 - \frac{C}{d}\right) \cdot \frac{\partial C}{\partial u}\right]. \quad (10)$$

Figure 7 Concentration profile for various values of time t^*, for MRVE = 2.5, RD = 0.9, CED = 17.12.

Equations (6) and (10), which were also established by Bouzon,[11] represent the general expression of the radial diffusion through a sphere with consequent change in dimensions. These equations generalize the second Fick's law for radial diffusion in a sphere. This law becomes a particular case when the volume of transferred liquid is negligible, as $r \to u$ and $\left(1 - \dfrac{C}{d}\right) \to 1$:

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \cdot \frac{\partial}{\partial r}\left[r^2 \cdot D \cdot \frac{\partial C}{\partial r}\right]. \tag{11}$$

Constant Diffusivity Case

Upon replacing the dimensionless variables u/R, r/R, $D \cdot t/R^2$, and C/d by the notations u, r, t, and C, the general set of equations is obtained

$$\frac{\partial r}{\partial u} = \frac{u^2}{r^2} \cdot (1 - C)^{-1} \tag{6'}$$

$$\frac{\partial}{\partial t}\left[(1 - C)^{-1} \cdot C\right] = \frac{1}{u^2} \cdot \frac{\partial}{\partial u}\left[\frac{r^4}{u^2} \cdot (1 - C) \cdot \frac{\partial C}{\partial u}\right]. \tag{10'}$$

By using these dimensionless variables, the curves are not dependent on the values of R, D, and d. Therefore the following values are taken for drawing the curves: $R = 1$, $D = 1$, $d = 1$.

For the stage of absorption these curves depend on a unique parameter, the constant concentration on the surface, CEA, which can also be defined by the maximum relative volume expansion (MRVE):

$$\beta = \left(1 - \frac{\text{CEA}}{d}\right)^{-1}. \tag{12}$$

But for the stage of desorption, the curves also depend on two other parameters: the initial profile of desorption, which is a function of the immersion duration, and the ratio of desorption, RD, which is a function of the surrounding volume, V, and of the partition coefficient, K.
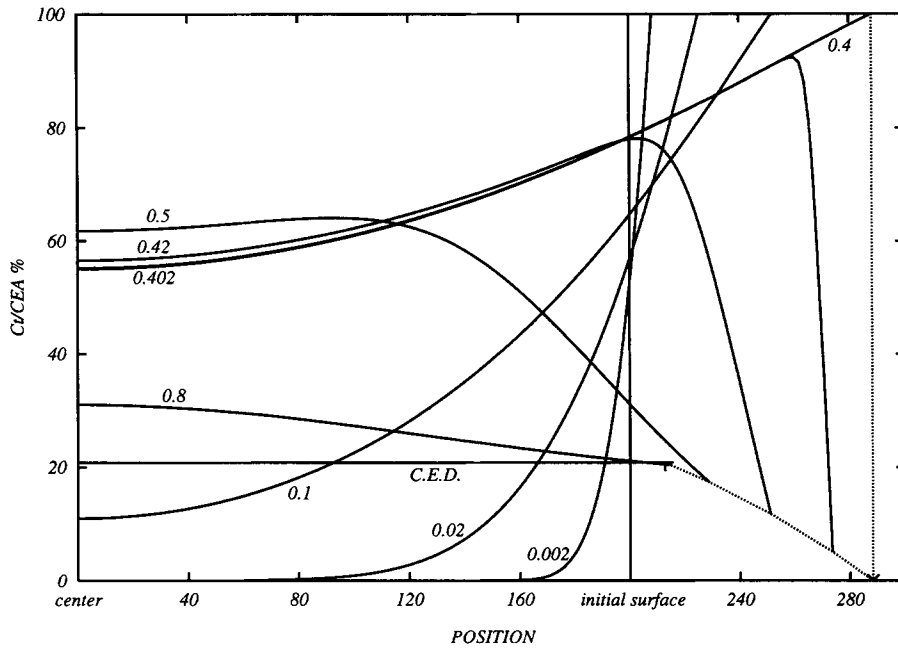
Boundary Conditions

Absorption

As soon as the process starts, the surface concentration of the diffusing liquid is equal to the concentration required in the bead to maintain equilibrium with the constant concentration in the surrounding:

$$C(R, t) = \text{CEA} \quad \text{with} \quad \text{CEA} = k \cdot C_{\text{ext}} = k \cdot d, \tag{13}$$

k being the partition coefficient for the absorption. Its value is:

$$k = \frac{\text{CEA}}{d} = 1 - \frac{1}{\beta}. \tag{14}$$

Figure 8 Concentration profile for various values of time t^*, for MRVE = 5.0, RD = 0.9, CED = 20.52.

Desorption

As the surrounding fluid is of finite volume, V, and strongly stirred, the concentration of the diffusing substance in the fluid is uniform and equal to

$$C_{ext,t} = \frac{M_t}{V}$$

where M_t is the amount of the diffusing substance released from the polymer in the surrounding up to time t. The concentration on the surface of the polymer is

$$C(R, t) = K \cdot C_{ext,t} \qquad (15)$$
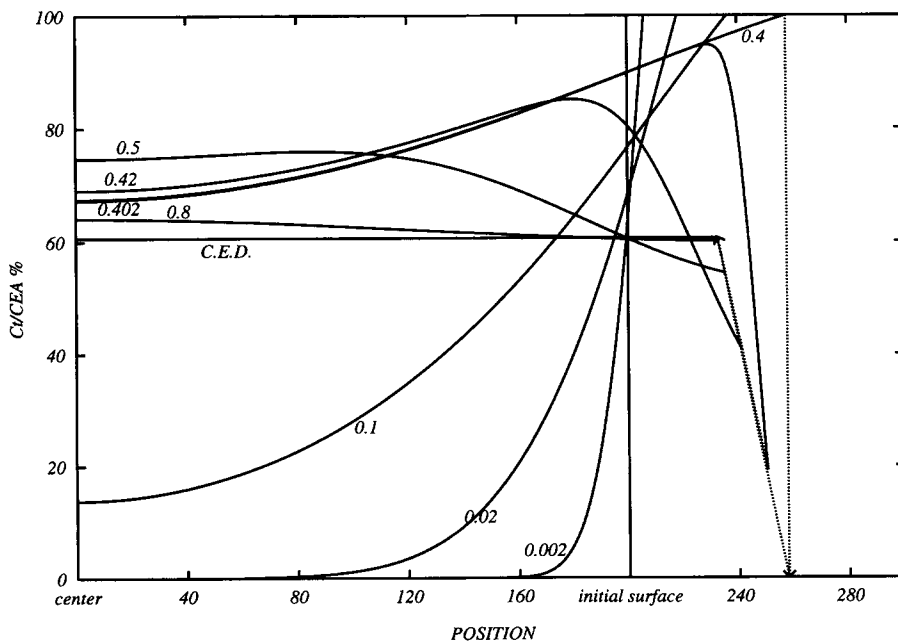
Figure 9 Concentration profile for various values of time t^*, for MRVE = 2.5, RD = 0.5, CED = 60.67.

K being the partition coefficient for the desorption. Thus is obtained

$$C(R, t) = K_V \cdot M_t \quad \text{with} \quad K_V = K/V. \quad (16)$$

There is also

$$M_t = \text{MPI} - \text{MP}_t, \quad (17)$$

where MPI is the amount contained in the bead at the end of immersion, which is also that at the beginning of desorption and MP_t is the amount of liquid contained in the bead at time t.

Calculation of K_v

At the final equilibrium of desorption the concentration is uniform in the bead, then

$$K_V \cdot M_\infty = C_\infty = \frac{\text{MP}_\infty}{VB_\infty} = \frac{\text{MP}_\infty}{VB_c + \text{MP}_\infty/d} \quad (18)$$

where VB_c is the canonical volume of the bead and MP_∞ is the amount of the diffusing liquid remaining in the bead at the final equilibrium of desorption.

The ratio of desorption is defined as

$$\text{RD} = \frac{M_\infty}{\text{MPI}} \quad (19)$$

Then

$$M_\infty = \text{RD} \cdot \text{MPI}, \quad \text{MP}_\infty = (1 - \text{RD}) \cdot \text{MPI}. \quad (20)$$

Finally eq. (16) allows one to obtain:

$$K_V = \frac{1 - \text{RD}}{\text{RD} \cdot \left[VB_c + \dfrac{(1 - \text{RD}) \cdot \text{MPI}}{d} \right]}. \quad (21)$$

Concentration at Final Equilibrium of Desorption

Equation (15) gives

$$C_\infty = K_V \cdot M_\infty = K_V \cdot \text{MPI} \cdot \text{RD}. \quad (22)$$

With eq. (14) the ratio is obtained

$$\text{CED} = \frac{C_\infty}{\text{CEA}}$$

$$= \frac{(1 - \text{RD}) \cdot \text{MPI}}{\left[VB_c + \dfrac{(1 - \text{RD}) \cdot \text{MPI}}{d} \right] \cdot \left(1 - \dfrac{1}{\beta} \right) \cdot d}. \quad (23)$$

Numerical Treatment

As the numerical model for the radial diffusion with the change in dimensions has already been established in the case of a constant concentration on the surface,[12] only the main results are given.

The radius of the liquid-free sphere is divided into N intervals of equal thickness Δu, and the radial abscissa, u, of each obtained point is associated with an integer j:

$$u = j \cdot \Delta u \quad \text{with} \quad 0 \le j \le N$$

$$\text{and} \quad \Delta u = \frac{R}{N}. \quad (24)$$

At time t, the radial abscissa associated with j becomes r_j, because of the presence of the liquid. Its value is given by:

$$r_j^3 \cdot \left(\frac{N}{R} \right)^3 = \frac{1}{8} \left(1 - \frac{C_0}{d} \right)^{-1} + \sum_{i=1}^{j-1} \left(3i^2 + \frac{1}{4} \right) \left(1 - \frac{C_i}{d} \right)^{-1}$$

$$+ [j^3 - (j - 0.5)^3] \left[1 - \frac{C_{j-0.25}}{d} \right]^{-1}$$

$$\text{for} \quad 1 \le j \le N. \quad (25)$$

Within Sphere (1 ≤ j ≤ N − 1)

The volumes of the spherical membrane limited by the canonical abscissae $(j - 0.5)\Delta u$ and $(j + 0.5)\Delta u$, at the moments t and $t + \Delta t$, are noted Vj and VNj, respectively, and the respective amounts of liquid located in this membrane are noted Bj and BNj:

$$BNj = VNj \cdot CNj$$

$$= Bj + 4\pi \cdot (G_{j+0.5} - G_{j-0.5}) \cdot \Delta t \quad (26)$$

with the function G

$$G_{j+0.5} = r_{j+0.5}^2 \cdot D_{j+0.5} \cdot \frac{C_{j+1} - C_j}{r_{j+1} - r_j}, \quad (27)$$

and the new concentration is:

$$CN_j = BN_j \cdot \left[4\pi \left(\frac{R}{N} \right)^3 \cdot \left(j^2 + \frac{1}{12} \right) + \frac{BN_j}{d} \right]^{-1}. \quad (28)$$

Center of Sphere (j = 0)

The new amount BN_0 in the small sphere of canonical radius $\Delta u/2$ is:

$$BN_0 = VN_0 \cdot CN_0 = B_0 + 4\pi \cdot G_{0.5} \cdot \Delta t, \quad (29)$$

and the new concentration CN_0:

$$CN_0 = BN_0 \cdot \left[\frac{4\pi}{3} \left(\frac{R}{2N} \right)^3 + \frac{BN_0}{d} \right]^{-1}. \quad (30)$$

Surface of Sphere (j = N)

For the stage of absorption, the concentration on the surface is constant, equal to the equilibrium concentration:

$$C_N = \text{CEA}. \quad (31)$$

For the stage of desorption, the concentration on the surface is constantly proportional to the concentration of the diffusing substance in the surrounding:

$$C_N = \frac{K}{V} \cdot M_t = K_V \cdot (\text{MPI} - \text{MP}_t) \quad (32)$$

Amount of Liquid Located in Sphere

The amount of diffusing substance located in the sphere at time t, MP_t, is obtained by integrating the concentration in the sphere at time t with respect to space:

$$\frac{\text{MP}_t}{4\pi} \left(\frac{N}{R} \right)^3 = \frac{C_0}{24} \left(1 - \frac{C_0}{d} \right)^{-1} + \sum_{j=1}^{N-1} \left(j^2 + \frac{1}{12} \right) C_j$$

$$\times \left(1 - \frac{C_j}{d} \right)^{-1} + \frac{N^3 - (N - 0.5)^3}{3} C'_N$$

$$\times \left(1 - \frac{C'_N}{d} \right)^{-1} \quad (33)$$

where C'_N is the mean concentration of the spherical membrane between the positions $N - 0.5$ and N. It is about equal to the concentration at the position $N - 0.25$ and is evaluated by linear interpolation:

$$C'_N = \tfrac{1}{4}(3C_N + C_{N-1}). \quad (34)$$

Stability of Calculation

The condition for stability of calculation is obtained by writing that the coefficient of concentration C_0 in eq. (29) is positive[13]:

$$\Delta t \leq \frac{R^2}{6N^2 \cdot \text{DM}} \quad (35)$$

where DM is the maximum value of the diffusivity.

RESULTS

We have chosen the case when the diffusivity is constant. Two kinds of results deserve mention: the kinetics of matter transferred along the two stages of absorption and desorption and the profiles of liquid concentration with the change in dimensions.

The kinetic curves are represented by the values of the ratio M_t/M_∞ as a function of the dimensionless time $t^* = (D \cdot t)/R^2$, where R is the radius of the liquid-free sphere.

The profiles of concentration are represented by the ratio $C_{r,t}/\text{CEA}$ (%) as a function of radial abscissa r, which varies with the swelling.

As we have previously shown,[14] these curves do not depend on the values of R, D, or d. They only depend on the parameters maximum relative volumic expansion β, duration of immersion, and desorption ratio RD. The calculations are made with the values $R = 1$, $D = 1$, $d = 1$, $N = 200$, $\Delta t = 4 \times 10^{-6}$. The parameter β takes the values 1.001, 1.25, 2.5, 5, and RD the values 0.1, 0.5, 0.75, 0.9, and 1 (complete desorption). In all cases the immersion is interrupted at the dimensionless time $t^* = 0.4$.

Kinetics of Matter Transfer for Process of Absorption–Desorption

The kinetics of matter transfer during the stages of absorption and desorption are drawn in Figs 1–4 for various values of the maximum relative volume expansion.

The following conclusions are worth noting:

1. The effect of the value of the maximum relative volume expansion, β, on the kinetics of absorption is significant, with the statement that the higher the value of β, the slower the kinetics of substance absorbed.
2. Following the above, equilibrium of absorption is nearly obtained when β is 1, but equilibrium is far from being reached when β is much higher than 1.
3. When β is close to 1 (1.001), meaning that the volume of liquid absorbed is very low, the kinetics calculated for absorption either with the numerical model or with the well-known solution of the Fick's law for radial diffusion

are the same:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2}$$

$$\times \exp\left(-\frac{n^2\pi^2}{R^2} Dt\right). \quad (36)$$

4. When β is higher than 1, the kinetics of desorption are faster than the kinetics of absorption, especially in the earlier stages of the process. The higher the β, the greater the difference.
5. For RD = 1 (complete desorption), the curves are the same as in the case of infinite volume of the surrounding atmosphere.[14]
6. Whatever the value of RD, desorption is very fast at the beginning of the process. For the small values of parameter RD, final equilibrium is reached very quickly.

Profiles of Substance Concentration and Change in Dimension

The profiles of concentration of the diffusing substance developed through the sphere are drawn for various values of β and RD in: Figure 5 (β = 1.001 and RD = 0.9); Figure 6 (β = 1.25 and RD = 0.9); Figure 7 (β = 2.5 and RD = 0.9); Figure 8 (β = 5.0 and RD = 0.9); Figure 9 (β = 2.5 and RD = 0.5).

The change in dimensions of the sphere is also shown. The concentration at time t, C_t, is expressed as a fraction of the maximum value of this concentration, attained when the solid is saturated with liquid. Various profiles are drawn for different values of the dimensionless number $t^* = D \cdot t/R^2$.

The following facts deserve mention:

1. In Figure 5, for β = 1.001, the change in dimensions is negligible. In the other figures when β > 1, an increase in the radius is observed during the stage of absorption, and a shrinkage appears with the desorption. Of course, the higher the maximum relative volume expansion β, the greater the change in dimensions.
2. Because of the very high value of the coefficient of matter transfer on the surface, the concentration of the diffusing substance on the solid surface reaches the value at equilibrium with the surrounding as soon as the process starts, that is, CEA, during the stage of absorption. At the initial time of desorption, the surface concentration immediately reaches the value zero and then it increases gradually up to the final equilibrium value C_∞ (represented by CED in the figures).

3. In all cases, equilibrium is not reached at the end of the stage of absorption after a value of $D \cdot t/R^2$ = 0.4, as the time selected for the stage of absorption is rather low.
4. Again, the concentration profiles of the diffusing substance are the same at the end of the stage of absorption and at the beginning of the following stage of desorption.

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