KINETIC OF LIQUID TRANSPORT IN ETHYLENE VINYL ACETATE BEAD

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ABSTRACT

In order to investigate the kinetic of the diffusion of a liquid in a polymer matrix, the study of the diffusion of the n-heptane in ethylene vinyl acetate is carried out. The polymer considered has a spherical shape. The kinetics of absorption and desorption of the liquid are carried out experimentally by weighing the bead at successive times. Thus the experimental curve is compared to the calculated curves using the analytical and numerical solutions. Two numerical solutions, based on finite differences are suggested:

1. Numerical solution for the bead without swelling
2. Numerical solution for bead with swelling and subsequent change in dimensions.

The second purpose seems being the better and give a good agreement with the experience since the diffusivity (experimental and calculated) are of the same magnitude.

Key word: diffusion, numerical analysis, ethylene vinyl acetate, polymer, matter transfer.

INTRODUCTION

When the n-heptane is in contact with the polymer, the liquid enters into the polymer by diffusing between the polymer chains. In the case of ethylene vinyl acetate, with the massic proportion of vinyl acetate equal to 28% and the melt index of 40 (EVAc 28-40), the polymer is in the caoutchouc state and the diffusion of liquid is of Fickian type¹ \( (M = k \sqrt{t}) \). Where \( M_t \) is the amount of liquid transferred at time \( t \). The process of matter transfer is controlled by transient diffusion.

The study of this phenomenon is of high interest since it helps us to understand and eventually to predict the liberation of drugs in stomach²,³,⁴,⁵ from the matrix of galenic shape. Results of this study can also apply to the liberation of fertilizer⁶,⁷,⁸ in the soil from a spherical geometrical form. The methodology followed in this study is the next:

1. The bead immersed in n-heptane is weighed at successive times and the curve \( M_t = f(\sqrt{t}) \) is drawn for short times \( (M_t < 0.2) \). From the slope of this curve we determine the experimental diffusivity.
2. Refine the diffusivity by the model calculations.
3. Compare the experimental curve \( M_t / M_\infty = f(t) \), where \( M_\infty \) is the amount of liquid in the bead at saturation, to those...
obtained by calculation for the analytical and numerical solutions.
4. Determine the profiles of concentration in both cases.

THEORETICAL
I.1 Analytical solution:
The followed assumptions are made:

- The shape of the bead is spherical and the radius of the sphere is constant during the entire process.
- The concentration at the surface reaches the concentration of equilibrium \( C_\infty \) as soon as the process begins

I.1.1 Mathematical treatment:
The matter transfer is considered to be radial through the sphere. The second Fick law expressed in spherical coordinates is of the form:

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right) = \frac{1}{r^2} \frac{\partial C}{\partial t}
\]

As the diffusivity \( D \) is considered to be constant the equation (1) becomes:

\[
\frac{\partial C}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right)
\]

We consider the following boundary conditions:

\[
t = 0 \quad 0 \leq r < R \quad C = C_m \quad \text{inside the sphere}
\]
\[
t > 0 \quad r = R \quad C = C_\infty \quad \text{surface of the sphere}
\]

Where \( C_m \) is the initial concentration and \( C_\infty \) is the constant concentration at the equilibrium. The mathematical resolution of equation (2) with respect to the above boundary conditions leads to the following profile of concentration:

\[
\frac{C(t) - C_m}{C_\infty - C_m} = 1 + \sum_{n=1}^{\infty} \frac{2R}{\pi n} \sin \frac{\pi n}{R} \exp \left( -\frac{D}{R^2} \frac{\pi^2 n^2}{4D} t \right)
\]

At the center of the sphere, as \( \frac{\sin x}{x} \to 1 \) when \( x \to 0 \), equation (5) becomes:

\[
\frac{C(t) - C_m}{C_\infty - C_m} = 1 + 2 \sum_{n=1}^{\infty} \frac{\pi n}{\pi^2 n^2} \exp \left( -\frac{D}{R^2} \frac{\pi^2 n^2}{4D} t \right)
\]

The amount of matter transferred up to time \( t \), \( M_t \), as a fraction of the corresponding quantity at infinite time, \( M_\infty \), is expressed in term of time as being:

\[
\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{1}{\pi^2 n^2} \exp \left( -\frac{D}{R^2} \frac{\pi^2 n^2}{4D} t \right)
\]

I.2 Numerical solution without swelling of bead:
Let us consider a radial transfer of liquid in the bead, the concentration at the surface reaches the value of the concentration at infinite time as soon as the process starts. In other words the matter transfer coefficient is infinite. The diffusivity \( D \) is taken to be constant. The radius of the sphere is divided into \( N \) intervals of the same thickness \( \Delta r \), then we obtain:

\[
R = N\Delta r
\]
\[
r = n\Delta r
\]

I.2.1 Concentration within the sphere:
The balance matter is evaluated during elapse of time \( \Delta t \), within the spherical membrane limited by the spherical surfaces of radius \((n-0.5)\Delta r\) and \((n+0.5)\Delta r\) with respect to the first Fick law:
I.2. Concentration at the center of the sphere:

Let us consider the little sphere of radius \( \frac{\Delta r}{2} \) with the same center as the sphere of radius \( R \). The balance matter through the spherical surface of radius \( \frac{\Delta r}{2} \) leads to:

\[
\frac{\Delta t}{2} \left[ \frac{2C}{\Delta r} + \frac{2C}{\Delta r} \right] A_n = V_n [C_{\text{in}} - C_n]
\]

Where

- \( A_n \) is the area of the spherical surface of radius \( r = n\Delta r \)
- \( \nabla C \) is the gradient of concentration at position \( n \)
- \( V_n \) is the volume of the spherical membrane of mean radius \( r \) and thickness \( \Delta r \)

\( C_{\text{in}} \) and \( C_n \) are respectively the new concentration after elapse of time \( \Delta t \), and the old concentration at the radial abscissa \( r = n\Delta r \). They are approximatively equal to the corresponding mean concentrations in the given spherical membrane.

The new concentration \( C_n \) after an increment of time \( \Delta t \) within the spherical membrane of mean radius \( n\Delta r \) is expressed in terms of the previous concentration at the same and adjacent positions.

\[
C_n = C_{\text{in}} = \frac{1}{M^3} \left( \frac{n-0.5}{n^4} (C_{n+1} - C_n) + \frac{n+0.5}{n^4} (C_{n-1} - C_n) \right)
\]

With the dimensionless number \( M \)

\[
M = \frac{b \Delta t}{D \Delta r^2}
\]

I.2.2 Concentration at the center of the sphere:

\[
\Delta t \left( \frac{2C}{r^2 \Delta r} + \frac{2C}{r^2 \Delta r} \right) A_n = V_n [C_{\text{in}} - C_n]
\]

\[
C_n = C_{\text{in}} \frac{6}{M} \left( C_0 - C_1 \right)
\]

I.2.3 Concentration at the surface of the sphere:

When the coefficient of matter transfer is high (infinite), the concentration at the surface of the sphere reaches its limit value as soon as the process starts, we have:

\[
C(R, t) = C_N = C_{\text{eq}}
\]

I.2.4 Amount of diffusing substance located in the sphere at time \( t \):

The amount of diffusing substance located in the sphere at time \( t \) is evaluated by integrating with respect to space the concentration within the sphere at this time.

\[
M_t = \int 4\pi r^2 C_{\text{eq}} \, dr
\]

By using the finite differences we obtain

\[
M_t = \frac{C_0}{4\pi (\Delta r)^3} + \sum_{n=1}^{N-1} \left( \frac{n^2}{2} + \frac{n}{2} \right) C_n
\]

I.3 Numerical solution with swelling of the bead:

Generally the matter transfer is accompanied by a swelling (absorption) or a shrinkage (desorption) of the bead\(^{10,11,12}\), a numerical solution is applied. As above the diffusivity is considered to be constant\(^{13,14,15,16}\).

The following assumptions are made:

1. Before immersion the bead of spherical shape is homogeneous and isotropic.
2. The diffusion of liquid in the bead is radial and controlled by the first Fick law.
3. The bead remains of spherical form during all the process.
4. The additivity of volume is equal to the volume of the bead free from liquid increased by the volume of liquid which enters in the bead.

5. The matter transfer coefficient is considered to be infinite in both absorption and desorption stages.

6. The internal pressure in the polymer due to its expansion is not considered.

7. The temperature in the bead and on its surface remains constant.

1.3.1 Mathematical treatment:

Let us consider a point within the bead, its radial abscissae is designed by \( u \), when the bead is free from liquid. After swelling at time \( t \) it becomes \( r(u, t) \).

The mathematical treatment of the swelling case leads to a generalized form of the second Fick law. That is expressed by:

\[
\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right) + \frac{1}{r^2} \frac{\partial C}{\partial r} \tag{16}
\]

If the variation of the volume of bead is proportional to the volume of the liquid which enters in the bead, equation (16) remains still valid. If \( \Delta V_{\text{bead}} = k \cdot V_{\text{liquid}} \), we replace in equation (16) \( d \) by \( d' = d / k \). which is the apparent density of liquid in the bead. The particular case \( k = 0 \) (\( r = u \)) leads to the well known second Fick law. In this case there is no change in the volume of the bead (\( \Delta V_{\text{bead}} = 0 \)) and equation (16) reduce to:

\[
\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right) \tag{17}
\]

The case \( k = 1 \) corresponds to the case of additivity of the volumes of the bead and the liquid \( d' \) becomes equal to the real density of the liquid.

1.3.2 Numerical solution:

The bead free from liquid is divided in \( N \) intervals of the same thickness \( \Delta u = R/N \). We consider the spherical membrane located between the radial abscissae \( r_{j-0.5} \) and \( r_{j+0.5} \). Its volume \( V_j \) at time \( t \) and its canonical volume (bead free from liquid) \( W_j \) are respectively:

\[
V_j = \frac{4}{3} \pi r_{j-0.5}^3 + \frac{4}{3} \pi r_{j+0.5}^3 \tag{18}
\]

\[
W_j = 4 \pi (\Delta u)^3 \left( r_{j-0.5}^3 + r_{j+0.5}^3 \right) \tag{19}
\]

The mathematical treatment leads to the following relations for the radial abscissae:

\[
r_{j-0.5} = \frac{R}{2N} \left( j - \frac{1}{2} \right) \tag{20}
\]

\[
\text{a) Concentration within the sphere:}
\]

The new concentration \( C_{Nj} \) at time \( t + \Delta t \) at radial abscissa \( r_j \) is given by:

\[
C_{Nj} = C_{Nj} + \frac{MN_j}{d} \left( C_{j-0.5} - C_{j+0.5} \right) \tag{21}
\]

Upon putting the function \( G \) as:

\[
G_{j-0.5} = \frac{r_{j-0.5}^3 - C_{j-1}}{r_j - r_{j+1}} \tag{22}
\]

The quantity \( MN \) is expressed by:

\[
MN_j = \frac{r_{j-0.5}^3 - C_{j-1}}{r_j - r_{j+1}} \tag{23}
\]
\[ M_{Nj} = V_j C_j + 4 \pi \Delta t (G_j + 0.5 - G_j - 0.5) \text{ with } 1 \leq j \leq N-1 \]

b) **Concentration at the center of the sphere**:

For the sphere centered on the origin of the bead and of radius \( \frac{\Delta r}{2} \), the new quantity of liquid after elapse of time \( \Delta t \) is:

\[ M_{N0} = V_0 C_0 + 4 \pi \Delta t G_{0.5} \]

And the new concentration is given by:

\[ CN_0 = \frac{M_{N0}}{V_0} + \frac{M_{Nj}}{d} \]

c) **Concentration at the surface of the sphere**:

The concentration at the surface of the bead reaches the equilibrium concentration as soon as the process begins. If \( M_{eq} \) is the quantity of liquid absorbed at the equilibrium, after an infinite time, the concentration at the surface of bead is expressed by:

\[ CN = \frac{M_{eq}}{V_0} + \frac{M_{eq}}{d} \]

d) **Amount of diffusing substance located in the sphere at time \( t \)**:

The amount of liquid located in the bead at time \( t \) expressed in terms of concentration is given by:

\[ \frac{M_i}{4\pi \Delta t} + \frac{1}{24} C \frac{C N}{d} + \frac{1}{12} C \frac{C N}{d} \]

Where \( C_N \) is given by:

\[ C_N = \frac{7}{4} C_{N-1} - \frac{3}{4} C_{N-2} \]

**EXPERIMENTAL**

The bead of ethylene vinyl acetate (Atochem France) is immersed in about 30 ml of n-heptane and the kinetic of absorption is followed by weighing the bead at intervals. After saturation the bead is taken out from the liquid and the kinetic of desorption by evaporation is followed as in the absorption stage. The ethylene vinyl acetate used in 28% in vinyl acetate and the melt index is 40. The final mass of heptane absorbed is equal to 0.0124 g which corresponds to a volume of 0.018 cm³.

**RESULTS AND DISCUSSIONS**

When the swelling is not considered, the experimental curve obtained by plotting the quantity \( \frac{M_t}{M_{\infty}} \) versus the square root of time \( t^{\frac{1}{2}} \),

\[ \frac{M_t}{M_{\infty}} = \frac{6}{R} \sqrt{\frac{D t}{\pi}} \text{ with } \frac{M_t}{M_{\infty}} < 0.2 \]

By considering the swelling, we note that the slope at the origin of the curve \( \frac{M_t}{M_{\infty}} = f \) is inversely proportional to the maximum relative volume expansion (MRVE):

\[ p = \frac{V_i}{V_f} \frac{6}{R} \sqrt{\frac{D}{\pi}} \]

Where \( V_i \) is the volume of the bead free from liquid and \( V_f \) is the final volume bead at equilibrium. This is illustrated in figure 1, where we have plotted \( \frac{M_t}{M_{\infty}} = \text{MRVE}. f \).
Fig. 1. Curves $\frac{M_t}{M_\infty} = f(t)$ for different swellings. Numbers on curves are the values of MRVEA.

We note that for $\frac{M_t}{M_\infty} \leq 20\%$ the slope of the curves is the same, independently of the values of MRVE. In this case the experimental diffusivity is calculated in the same manner but by using equation (31). By plotting the curve $\frac{M_t}{M_\infty} = f(t)$ for the experimental points, in the interval $0 \leq M_t/M_\infty \leq 20\%$. We determine the diffusivity from the slope at the origin. The different values of the diffusivity are gathered in table 1.

Table 1. Diffusivity determined from the slope at the origin of the experimental curve

| From equation (30) | From equation (31) |
|-------------------|-------------------|
| $D. 10^7$ (cm$^2$/s) | 1.20 3.18 |

The figures 2, 3, 4 show the experimental curve and those calculated by using respectively the analytical solution, the numerical solution without swelling and the numerical solution with swelling. We note that the third case agree well with the experiment. Table 2 gather the values of diffusivity obtained in three simulating cases.

Fig. 2. Curve $\frac{M_t}{M_\infty} = f(t)$ simulated by using the analytical solution.

Fig. 3. Curve $\frac{M_t}{M_\infty} = f(t)$ simulated by using the numerical solution without swelling.

Fig. 4. Curve $\frac{M_t}{M_\infty} = f(t)$ simulated by using the numerical solution with swelling.
The difference is well observed in the desorption stage. In the sorption stage of the analytical solution, particularly at the first times, the curves do not superpose. So the numerical solutions are better than the analytical one.

The profiles of concentration in case of numerical solution with swelling are plotted in figures 5 and 6. In case of sorption (fig.5), we note that the radius of the bead change from $R_i = 0.1902 \text{ cm}$ to $R_f = 0.2237 \text{ cm}$. Hence the swelling is $\Delta R = R_f - R_i = 0.0335 \text{ cm} \ (17.61\%)$ and the concentration within the bead becomes nearly homogeneous after twenty hours.

In the desorption stage we observe the shrinkage from $R_i$ to $R_f$, and the concentration within the bead tends to the profile after twelve hours.

### CONCLUSION

This study leads to a generalization of the second Fick law, it shows the importance of the swelling in the simulation of the diffusion kinetic. The study may be helpful to understand the diffusion of antibiotics in stomach, or the liberation of chemical fertilizer in soil. This can help us to control the liberation of diffusing substance and to avoid the toxic levels in each case. Other studies are carried on in the laboratory, with other diffusing substances and for different geometrical forms. The results will appear later.

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