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POSSIBLE INDIRECT MEASUREMENT OF DIFFUSION COEFFICIENT FROM MIGRATION KINETIC ESSAY OF FOOD PACKAGING

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Abstract: Diffusion coefficient is an important quantity that affects any migration process on food or nutritional systems. Special care has to be done to migration of undesirable substances from packaging into foods, if the diffusion is the only process involved in mass transfer. The Fick´s equation resolution permits to describe the kinetic of migration from polymer packaging into food or simulant, once it was given the correct contour and initial conditions. Another important quantity is the partition coefficient, which quantifies the relation between the final or equilibrium concentrations in polymer and that in the food or simulant. Here it is proposed a simple procedure, based on numerical resolution of the Fick´s equation, where the diffusion coefficient could indirectly be measured, if the kinetic of migration had been measured and the partition coefficient is known.

Keywords: diffusion, migration, packaging.

1. INTRODUCTION

When experimental determination is rather difficult or subject to large uncertainties, theoretical evaluation method has to be proposed. It is the case of many migration or diffusion studies that happens in food or nutritional systems.

The migration process could be described mathematically by an equation. This partial differential diffusion equation, known as Fick´s second law, is the following:

$$\frac{\partial}{\partial t} C = \frac{\partial}{\partial x}\left(D \frac{\partial}{\partial x} C \right) \qquad (1)$$

C is the concentration profile of the migrant substance and D is the diffusion coefficient.

It describes diffusion process, like the migration of specific substance from polymeric packaging into food. D depends on the kind of substance, on the medium where mass transport occurs, on temperature, etc.. So, mathematically speaking, it is a function of the position. This position dependence of D is not present in the most mathematical models used to simulate migration in food-packaging systems [1-2], but it is very important because it intrinsically depends on the microstructure of the medium the molecule is passing through.

The amount of mass of the migrant (substance that migrated) transferred from the polymeric matrix into the food or simulant[1] is mathematically described by the function *concentration profile*, which is a function of the position and time, see figure 1.

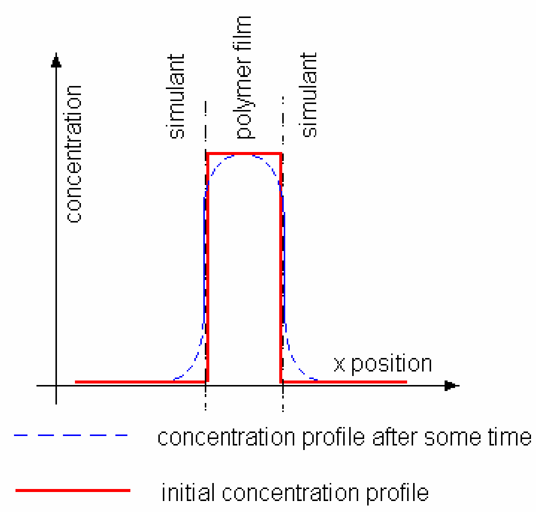

Fig. 1. Draft of the mathematical function "concentration profile" at two instants, supposed to be subject to diffusion process. Full line is the initial concentration profile and dotted line is the profile at some after time.

The knowledge of C at any time and at any position, nothing more than the solution of equation 1, permits to know everything about the migration process. As an example of useful application, it is possible to estimate the time interval when the concentration into the food will achieve specific values (sometimes prohibitive), and this permits to know if the migration limits, established according to Legislation [3], would be overtaken by that food packaging system.

As D is so important in diffusion process, it dictates the time evolution of the concentration profile.

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[1] Simulant is a substance that has a more simple composition than some food or medicine, and is used to substitute this food in migration tests. In general, simulants show a simple chromatogram (or any other characterization spectrum) and have a diffusion behavior like that of the food or medicine intended to be analyzed.

The amount migrated or, mathematically speaking, the calculus integration of C in food or simulant, is known as *kinetic of migration*.

It is known that after a very extensive time interval, equilibrium is achieved and migrant concentrations at food, C_f, and at packaging, C_p, are not the same. The quotient $k=C_f/C_p$ is the quantity known as partition coefficient. Interesting studies on k have been going on [4].

A very important experimental essay to measure the kinetic of migration is based on total immersion of pieces of polymer packaging into simulant, at normative time intervals and temperatures. After these conditions of contact, the piece is removed from the simulant and the migrated amount is quantified, normally by gas chromatography [5-7]. This kinetic of migration depends on the geometry of the sample and temperature, beside other parameters.

In this work it is presented a procedure to make an indirect measurement of D, based on the results of the migration kinetic experiment and computational simulation. The numerical procedure to simulate the kinetic of migration of some substance from polymeric films into food simulant has D as a parameter to be varied until the migration kinetic curve fits the analytical chemistry experimental results. When this fitting is achieved, the indirect measurement of the diffusion coefficient of the specific substance in that polymer film is completed. These films are intended to be used for foodstuffs packaging, but this procedure could be used to another film diffusion situations. The first motivation of the creation of this procedure was to study modification of the kinetic of migration caused by food irradiation [8].

2. SIMULATION PROCEDURE

It was used finite differences [9] and equation 1 is solved by Manzoli et al. by a numerical simulation procedure [10-12].

The numerical solution uses a non-uniform mesh of points for the discretization of x domain. The density of points is higher close to interfaces. Each point is labeled as illustrated in Figure 2.

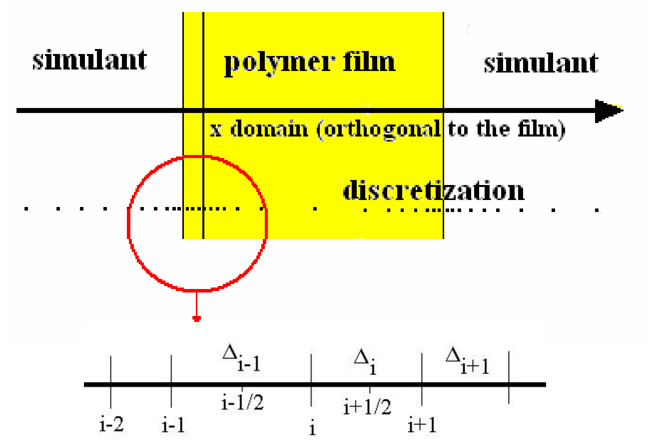

Fig. 2. Sketch of the polymer film/simulant system. The continuous x domain is shifted to a finite number of points (discretization). Below: indication of the interval and point labels.

In order to numerically solve Fick´s equation, Eq.(1), the x domain was discretized in n points by using a three-point finite difference scheme, which generates the following form for the left side of Eq.(1):

$$\begin{aligned}
&\frac{d}{dx}D(x)\frac{d}{dx}C(x)\overset{N}{\cong}\frac{d}{dx}D(x)\left[\frac{C_{i+1/2}-C_{i-1/2}}{\Delta_i+\Delta_{i-1}}2\right]=\\
&=\left(D_{i+1/2}\frac{C_{i+1}-C_i}{\Delta_i}-D_{i-1/2}\frac{C_i-C_{i-1}}{\Delta_{i-1}}\right)\frac{2}{\Delta_i+\Delta_{i-1}}=\\
&=\left(\frac{2D_{i+1/2}}{\Delta_i(\Delta_i+\Delta_{i-1})}\right)C_{i+1}+\\
&-\left(\frac{2D_{i+1/2}}{\Delta_i(\Delta_i+\Delta_{i-1})}+\frac{2D_{i-1/2}}{\Delta_{i-1}(\Delta_i+\Delta_{i-1})}\right)C_i+\\
&+\left(\frac{2D_{i-1/2}}{\Delta_{i-1}(\Delta_i+\Delta_{i-1})}\right)C_{i-1}=OC
\end{aligned} \tag{2}$$

Δ_i (or ΔX_i) is the non-constant distance between successive points i. D is diffusion coefficient. Operator O condenses notation.

After some algebraic manipulations of operator O, Eq.(1) becomes:

$$\left(1-\frac{O\Delta t}{2}\right)C_{t+\Delta t}=\left(1+\frac{O\Delta t}{2}\right)C_t=f_i \tag{3}$$

The f_i is a known value, easily calculated, and Δt is the time step.

Opening the O operator, Eq.(3) becomes:

$$C_{t+\Delta t}(x_i)-\Delta t\left[\begin{array}{l}
\dfrac{D_{i+1/2}}{\Delta x_i(\Delta x_i+\Delta x_{i-1})}C_{t+\Delta t}(x_{i+1})+\\
-\left(\dfrac{D_{i+1/2}}{\Delta x_i(\Delta x_i+\Delta x_{i-1})}+\dfrac{D_{i-1/2}}{\Delta x_{i-1}(\Delta x_i+\Delta x_{i-1})}\right)C_{t+\Delta t}(x_i)+\\
+\dfrac{D_{i-1/2}}{\Delta x_{i-1}(\Delta x_i+\Delta x_{i-1})}C_{t+\Delta t}(x_{i-1})
\end{array}\right]$$

$$= f_i \tag{4}$$

Eq.(4) is the time evolution of the Concentration function, C. It is a tridiagonal system of n linear equations, where n is the total number of points, which is easily solved.

Partition coefficient is supposed to act as a factor multiplying the initial concentration profile, present inside the polymer packaging. In order to calculate or made an indirect measurement of diffusion coefficient of the migrant inside the polymer, D_p, the following amounts had to be determined previously, and used as input variables in the simulation. These inputs are: initial concentration profile, partition coefficient, diffusion coefficient of the migrant inside food or simulant, thickness of the polymer film. The algorithm is simple: it is varied D_p until the kinetic of migration fits the experimental results. Of course, this algorithm could be used to determine (measure) any of the cited input quantities, if the others, including D_p, were known.

Examples of Application

Diffusion Coefficient of UV absorber in PET

Tinuvin P is an additive substance present into PET bottles of olive oil, as an example, that blocked ultra-violet rays. It migrates to the olive oil or to n-heptane, its simulant. Figure 3 shows the migration kinetic of this substance [12].

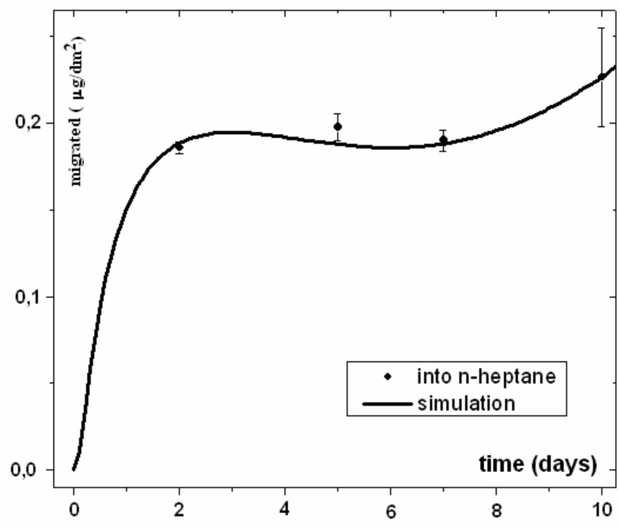

Fig. 3: Experimental results for migration of Tinuvin P into n-heptane and migration kinetic simulation curve (solid).

Diffusion coefficient of Tinuvin P inside PET was calculated and gave the value 4.3x10^2 µm^2/day and inside n-heptane was 5x10^5 µm^2/day.

Diffusion Coefficient of Plasticizer in PVC

In figure 4, it is shown an example of kinetic of migration of a phtalate from a flexible PVC packaging into solid cheese, possible to be measured by total immersion and gas chromatography. Points indicated supposed experimental results, based on tables and producers of packaging information. Curves are the simulated ones. Only the solid curve fits the experimental results. So, this procedure measured the diffusion coefficient of this phtalate inside the PVC as 14 µm^2/s. Some variations from this value cause the other migration kinetics shown.

3. CONCLUSION

Simulation of migration could be a cost- and timesaving alternative to migration experiments. This procedure can be used to make indirectly measurements of diffusion coefficient of migrants in the polymer matrix of a packaging. Once knowing this coefficient, predicting migration can be achieved, for any food-packaging systems made by that polymer and containing that migrant.

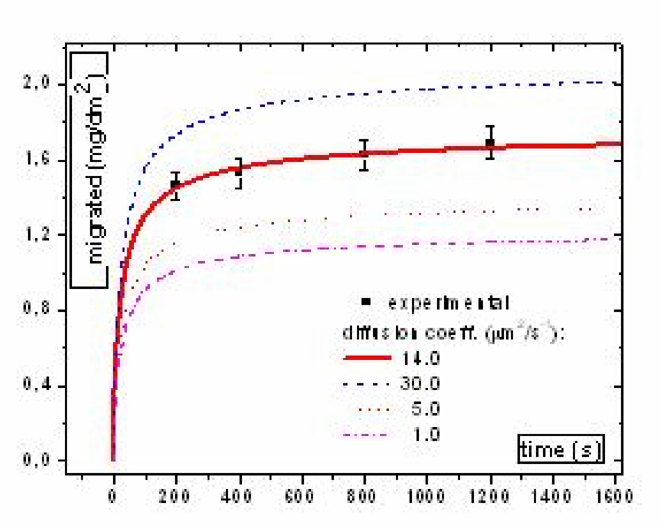

Fig. 4. Kinetic of migration of DEHP from flexible PVC packaging into solid cheese. Points are supposed experimental results, from total immersion contact and gas chromatography essay. Lines are simulated results.

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