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A SPECIAL CASE OF DIFFUSION WITH MOVING BOUNDARY

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Abstract—The penetration distance of a diffusant from a thoroughly mixed medium into a second, polymeric medium with moving boundary is calculated by means of a balance equation and is compared with experimental values.

NOMENCLATURE

- a, position of boundary;
- a_0, position of boundary at time $t = 0$;
- A, area;
- c, concentration of diffusant;
- c_a, concentration of diffusant at boundary;
- c_{a0}, initial concentration in the first, limited medium;
- c_0, constant concentration at boundary;
- D, diffusivity of diffusant;
- M, total amount of diffusant;
- n, exponent;
- q, penetration distance of diffusant;
- Q, total amount of diffusant normalized by area [equation (2)];
- t, time;
- v, moving velocity of boundary;
- x, distance from origin;
- y, distance from boundary.

FORMULATION

THE DIFFUSION of a solute is considered which is proceeding from a first, limited medium into a second, unlimited medium. The total amount of diffusant is constant and initially restricted to the first medium. The boundary between both media may migrate with constant velocity into the direction of the second medium. Within the first medium, equipartition of the diffusant is maintained, e.g. by rapid diffusion or convection, throughout the equilibration process. Within the second medium, a cubic profile of concentration is supposedly at steady-state, see [1] (Fig. 1),

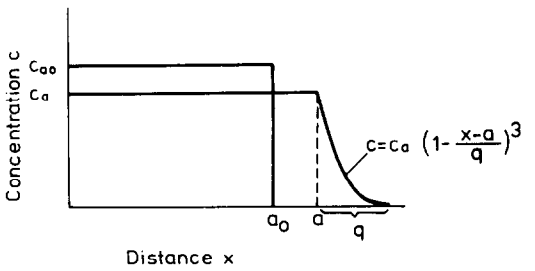

FIG. 1. Concentration distribution with moving boundary.

$$c(t) = c_a(t)\left[1 - \frac{x - a(t)}{q}\right]^3 \quad \text{for} \quad x \geqslant a_0 \qquad (1)$$

with

$$a(t) = a_0 + vt$$

and

$$v = \frac{\mathrm{d}a}{\mathrm{d}t}.$$

As to the total amount, normalized by area, we then have

$$Q = \frac{M}{A} = c_a(t) \cdot a(t) + \int_{a(t)}^{a(t)+q} c(t)\,\mathrm{d}x, \qquad (2)$$

and following integration

$$Q = c_a(t)\left[a(t) + \frac{q}{4}\right]. \qquad (3)$$

In an infinitesimal boundary layer advancing into positive x-direction, the equilibrium condition for the amount of diffusant exchanged per unit area and per unit time is: the amount of substance diffusing into the boundary layer from the left, augmented by the amount of substance gathered by the advance of the boundary layer, is equal to the amount of substance diffusing out to the right. In mathematical terms:

$$-D\frac{\partial c(a_-,t)}{\partial x} + vc(a_+,t) = -D\frac{\partial c(a_+,t)}{\partial x}. \qquad (4)$$

Because of the even concentration profile of diffusant within the first (left) medium, we have:

$$D\frac{\partial c(a_-,t)}{\partial x} = 0. \qquad (5)$$

Therefore, formula (4) assumes the simplified form:

$$vc(a_+,t) + D\frac{\partial c(a_+,t)}{\partial x} = 0 \qquad (6)$$

which states: the amount of substance gathered by the advancing boundary layer is, in equilibrium, diffusing totally into advancement direction, i.e. it follows the concentration gradient.

Substitution of (1) into (6) results in:

$$q = \frac{3D}{v}, \tag{7}$$

which constitutes a connection between the penetration distance of a diffusant, its diffusivity, and the advancement of the boundary.

The concentration of the diffusant can then be calculated from (3) and (7) to give:

$$c_a(t) = \frac{Q}{a(t) + \frac{3D}{4v}}. \tag{8}$$

DISCUSSION

The presented case of diffusion with moving boundary is of significance, e.g. for the dissolution of polymeric substances. According to Peterlin [2], the concentration profile within polymers is approaching the exponential limit distribution

$$c = c_0 \exp - \frac{yv}{D}. \tag{9}$$

The concentration within the first medium of the diffusant is thus supposed to be constant (c_0) throughout the equilibration process. The present considerations are relating to the case, close to practice, that the concentration within the first medium is declining because of mass transfer across the boundary.

Figure 2 points out an experimental example of diffusion of the physiologically inert, radioactively labelled ^{51}Cr-EDTA into a dissolving fibrin clot from human plasma, containing 1000 I.U. of the fibrinolytic streptokinase per millilitre. The experimental design permits to scan the radioactivity distribution from outside, thus circumventing concentration measurements [3]. The apparent drop in radioactivity on the plasma-side before the boundary, however, is geometrically due to the finite diameter of the detector-orifice. In fact, the radioactivity within the first medium is always equipartite.

Given a ^{51}Cr-EDTA diffusivity of 6×10^{-6} cm^2 s^{-1} and a boundary migration velocity of 6.9×10^{-6} cm s^{-1}, the resulting exponential limit distribution will assume a half band width of 0.6 cm, according to equation (9). Furthermore, equation (7) states the penetration depth to amount to 2.6 cm, corresponding to an exponential limit distribution $c/c_0 = 0.05$. Figure 2 demonstrates conformity between experimental and calculated values, where it has additionally to be taken into account, however, that the measurement accuracy will lessen with decreasing count rate, and that an equilibrium has still to be built up for the diffusion into the polymeric medium.

With regard to the fact that a more rigorous mathematical treatment of Stefan problems—which include the present case—is an intricate enterprise (compare e.g. [4]), there is nevertheless remarkable conformity of the submitted simple calculations based on balance equations with distributions that are experimentally determined or calculated in another way.

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APPENDIX

The choice of a cubic concentration profile in (1) may at first seem rather arbitrary, particularly since quadratic statements are known too [5]. Subsequently an attempt will be made to establish theoretically the choice of the exponent n.

The starting point is the generalized equation (1):

$$c(t) = c_a(t)\left[1 - \frac{x - a(t)}{q}\right]^n, \quad x \geqslant a_0. \tag{10}$$

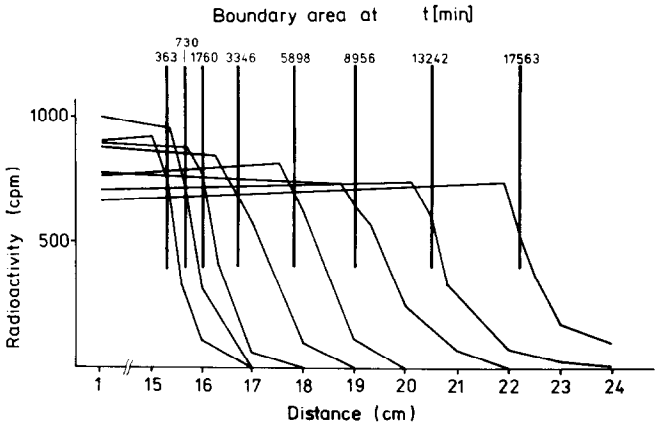

FIG. 2. Diffusion of ^{51}Cr-EDTA from human plasma, containing 1000 I.U. of streptokinase/ml, (on the left of boundary) into a dissolving fibrin clot (on the right of boundary).

Putting $c_a(t)$, respectively c_0 in (9), equal to unity and fixing the coordinates' origin to the moving boundary, the simplified equation

$$c(t) = \left(1 - \frac{y}{q}\right)^n \tag{11}$$

can be compared with the exponential concentration profile (9) (see Peterlin [2])

$$c(t) = \exp - \frac{vy}{D}. \tag{12}$$

Optimal conformation of these two curves ought to be attained when the area between them reaches a minimum:

$$\int_0^q \exp - \frac{vy}{D}\,dy - \int_0^q \left(1 - \frac{y}{q}\right)^n dy = \text{minimum!} \tag{13}$$

Prior substitution of (11) into (6) yields

$$q = \frac{nD}{v}. \tag{14}$$

With regard to this relation, the calculation of the minimum problem results in the equation

$$\exp(n) = (n+1)^2 \tag{15}$$

with the approximate solution $n \approx 2.5$.

Equations (10) and (11) will thus assume the respective forms:

$$c(t) = c_a(t)\left[1 - \frac{x - a(t)}{q}\right]^{2.5}, \quad x \geqslant a_0 \tag{16}$$

and

$$q = \frac{2.5D}{v}. \tag{17}$$

In addition this implies the choice of a dimensionless number. If $qv/D < 2.5$, then, with moving boundary diffusion, equilibrium is not yet attained.

UN CAS SPECIAL DE DIFFUSION AVEC FRONTIERE MOBILE

Résumé—On calcule à partir d'une équation de bilan, la distance de pénétration d'un diffusant depuis un milieu parfaitement mélangé, dans un second milieu polymérique avec frontière mobile et on compare avec les valeurs expérimentales.

Zusammenfassung—Es wird die Eindringtiefe einer diffundierenden Substanz aus einer vollständig durchmischten Phase in eine zweite polymere Phase bei wandernder Grenzfläche mit Hilfe einer Bilanzgleichung berechnet und mit experimentellen Werten verglichen.

ЧАСТНЫЙ СЛУЧАЙ ДИФФУЗИИ С ПОДВИЖНОЙ ГРАНИЦЕЙ

Аннотация — На основе уравнения баланса рассчитана грубина проникновения диффузанта из тщательно перемешанной среды в другую, полимерную, среду с подвижной границей и проведено сравнение с экспериментальными данными.