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A Note on Diffusion in Finite Composite Media

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Mathematical expressions for diffusion in finite composite media were derived analytically. The fact that, contrary to infinite cases, the interface concentration drifts with time was confirmed. The time course of a finite composite system was displayed graphically.

Keywords——mathematical expression; finite composite media; diffusion; interface concentration; three dimensional display

In the course of studies on drug release from ointment bases, one encounters problems of diffusion in systems in which two media are present. If the system is infinite (infinite composite media), mathematical solutions to the problem have been given elsewhere.[1]

Suppose the region $x<0$ is of one medium in which the diffusion coefficient is D_1, and in the region $x>0$ the diffusion coefficient is D_2. In the simplest case, the initial conditions are that the region $x<0$ is at a uniform concentration C_0, and in $x>0$ the concentration is zero initially. If we write C_1 for the concentration in $x<0$ and C_2 in $x>0$, the boundary conditions at the interface $x=0$ may be written

$$C_2/C_1=k, \quad x=0 \tag{1}$$

$$D_1\partial C_1/\partial x=D_2\partial C_2/\partial x, \quad x=0 \tag{2}$$

where k is the ratio of the uniform concentration in the region $x>0$ to that in $x<0$ when final equilibrium is attained. The condition (2) expresses the fact that there is no accumulation of diffusing substance at the boundary. Solutions are expressed as

$$C_1=\frac{C_0}{1+k(D_2/D_1)^{1/2}}\left[1+k(D_2/D_1)^{1/2}\ \mathrm{erf}\frac{|x|}{2\sqrt{D_1t}}\right] \tag{3}$$

$$C_2=\frac{kC_0}{1+k(D_2/D_1)^{1/2}}\mathrm{erfc}\frac{x}{2\sqrt{D_2t}} \tag{4}$$

where $\mathrm{erf}(x)=\frac{2}{\sqrt{\pi}}\int_0^x e^{-y^2}\,dy$ and $\mathrm{erfc}(x)=1-\mathrm{erf}(x)$.

It may be noted that, as diffusion proceeds, the concentrations at the interface, $x=0$, remain constant at the values

$$C_1=\frac{C_0}{1+k(D_2/D_1)^{1/2}}, \quad C_2=\frac{kC_0}{1+k(D_2/D_1)^{1/2}}. \tag{5}$$

Even if the system is finite, the concentrations at the interface will have the values of (5) for small t. In general, if t is small, solutions for an infinite system approximate those for finite systems. At steady state, $t=\infty$, however, it is apparent that the interface concentrations of finite systems are to have the values

$$C_1=\frac{C_0}{1+k(L_2/L_1)}, \quad C_2=\frac{kC_0}{1+k(L_2/L_1)}. \tag{6}$$

where L's are the respective thicknesses of the media. Therefore, unless $(D_2/D_1)^{1/2}$ and (L_2/L_1) are equal, the interface concentrations must drift as time passes.

The aim of this note is to derive mathematical expressions for finite composite systems and confirm the drift of interface concentrations.

Theoretical

As shown in Fig. 1, we take the finite region $-h<x<l$, of which $-h<x<0$ is of one medium and $0<x<l$ is of another. We write D_1 and C_1 for the diffusion coefficient and concentration of diffusing substance in the region $-h<x<0$, and D_2, C_2 for the corresponding quantities in $0<x<l$. The differential equations to be solved are

$$\frac{\partial C_1}{\partial t}=D_1\frac{\partial^2 C_1}{\partial x^2},\quad -h<x<0,\quad t>0 \tag{7}$$

$$\frac{\partial C_2}{\partial t}=D_2\frac{\partial^2 C_2}{\partial x^2},\quad 0<x<l,\quad t>0. \tag{8}$$

If we assume that there is no accumulation of diffusing substance at the interface, $x=0$, and no diffusion through the ends of the system, $x=-h$ and $x=l$, the boundary conditions are equations (1) and (2) above, and (9) and (10) below.

$$D_1\partial C_1/\partial x=0,\quad x=-h,\quad t>0 \tag{9}$$

$$D_2\partial C_2/\partial x=0,\quad x=l,\quad t>0. \tag{10}$$

The initial conditions are that the region $-h<x<0$ is at a uniform concentration, C_0, and in $0<x<l$ the concentration is zero initially.

$$C_1=C_0,\quad -h<x<0,\quad t=0 \tag{11}$$

$$C_2=0,\quad 0<x<l,\quad t=0 \tag{12}$$

Problems on diffusion in composite media are usually best solved by the Laplace transformation method.[2] For the system described above, the subsidiary equations are

$$\frac{\mathrm{d}^2\left(\bar{C}_1-\frac{C_0}{s}\right)}{\mathrm{d}x^2}-q_1{}^2\left(C_1-\frac{\bar{C}_0}{s}\right)=0,\quad -h<x<0 \tag{13}$$

$$\frac{\mathrm{d}^2\bar{C}_2}{\mathrm{d}x^2}-(rq_1)^2\bar{C}_2=0,\quad 0<x<l \tag{14}$$

where $q_1=(s/D_1)^{1/2}$ and $r=(D_1/D_2)^{1/2}$.
These are to be solved with

$$D_1\frac{\mathrm{d}\bar{C}_1}{\mathrm{d}x}=D_2\frac{\mathrm{d}\bar{C}_2}{\mathrm{d}x},\quad k\bar{C}_1=\bar{C}_2,\quad x=0 \tag{15}$$

$$\frac{\mathrm{d}\bar{C}_1}{\mathrm{d}x}=0,\quad x=-h \tag{16}$$

$$\frac{\mathrm{d}\bar{C}_2}{\mathrm{d}x}=0,\quad x=l \tag{17}$$

A solution of equation (13) is

$$\bar{C}_1=\frac{C_0}{s}+A_1\cosh(q_1x)+B_1\sinh(q_1x)$$

and a solution of equation (14) is

$$\bar{C}_2=A_2\cosh(rq_1x)+B_2\sinh(rq_1x)$$

The unknowns, A's and B's, are found from equations (15) through (17) and we get finally

$$\bar{C}_1=\frac{C_0}{s}-\frac{kC_0\sinh(lrq_1)\cosh[q_1(x+h)]}{s[r\sinh(hq_1)\cosh(lrq_1)+k\cosh(hq_1)\sinh(lrq_1)]} \tag{18}$$

$$\bar{C}_2=\frac{rkC_0\sinh(hq_1)\cosh[rq_1(x-l)]}{s[r\sinh(hq_1)\cosh(lrq_1)+k\cosh(hq_1)\sinh(lrq_1)]} \tag{19}$$

To evaluate C_1 and C_2 we can use the expansion procedure.[3)]

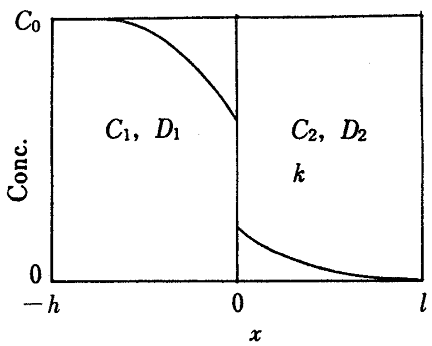

Fig. 1. Diagrammatic Representation of a Finite Composite System $k=C_2/C_1$ ($x=0$)

```
PHI=  1.40334824758

 D1T       C(X=0)

  .010    .3333333333
  .020    .3333335881
  .030    .3333531365
  .040    .3335142009
  .050    .3340290677
  .060    .3350632976
  .070    .3366783757
  .080    .3388531208
  .090    .3415213044
  .100    .3445999556
  .200    .3841627692
  .300    .4221708043
  .400    .4539062057
  .500    .4800168677
  .600    .5014644746
  .700    .5190785415
  .800    .5335439741
  .900    .5454235844
 1.000    .5551796082
 2.000    .5937456520
 3.000    .5991272528
 4.000    .5998782147
 5.000    .5999830058
 6.000    .5999976286
 7.000    .5999996691
 8.000    .5999999538
 9.000    .5999999936
10.000    .5999999991
```

Fig. 3. Computer Output after Running the Program shown in Fig. 2

```
 10 REM .......................
 20 REM   CALCULATION OF PHI
 30 REM   BY NEWTON METHOD
 40 REM .......................
 50 DEF FNF(X) = 3*SIN(2*X)-SIN(
    X)
 60 DEF FND(X) = 6*COS(2*X)-COS(
    X)
 70 REM
 80 P1=1.5
 90 P9=FNF(P1)/FND(P1)
100 P1=P1-P9
110 IF ABS(P9)>.0000000001 THEN
    90
120 PRINT "PHI= ";P1 @ PRINT
130 REM .......................
140 REM    CALCULATION OF
150 REM    INTERFACE CONC.
160 REM .......................
170 DEF FNS(X)
180 B1=1.75*TAN(1.5*X)
190 B2=1.25*COT(.5*X)
200 FNS=EXP(-(X^2*T))/(X*(B1-B2)
    )
210 FN END
220 REM
230 DEF FNC(T)
240 S1=0
250 P2=PI*2
260 N=-1
270 N=N+1
280 S9=0
290 P8=N*P2
300 B9=P8+P1
310 S9=S9+FNS(B9)
320 B9=P8+PI
330 S9=S9+FNS(B9)
340 B9=P8+P2-P1
350 S9=S9+FNS(B9)
360 B9=P8+P2
370 S9=S9+FNS(B9)
380 S1=S1+S9
390 IF ABS(S9)>.0000000001 THEN
    270
400 FNC=.6+S1*2
410 FN END
420 REM
430 PRINT " D1T     C(X=0)"
440 PRINT
450 IMAGE DD.DDD,2X,D.DDDDDDDDDD
460 FOR T=.01 TO .09 STEP .01
470 PRINT USING 450 ; T,FNC(T)
480 NEXT T
490 FOR T=.1 TO .9 STEP .1
500 PRINT USING 450 ; T,FNC(T)
510 NEXT T
520 FOR T=1 TO 10
530 PRINT USING 450 ; T,FNC(T)
540 NEXT T
550 END
```

Fig. 2. BASIC Program for the Interface Concent ration Time Course

$$C_1=\frac{hC_0}{h+kl}+2kC_0\sum_{m=1}^{\infty}\frac{\sin(h\beta_m)\cos[(x+h)\beta_m]e^{-D_1\beta_m^2t}}{B_m} \quad (20)$$

$$C_2=\frac{khC_0}{h+kl}-2rkC_0\sum_{m=1}^{\infty}\frac{\sin(h\beta_m)\cos[r(x-1)\beta_m]e^{-Dt\beta_m^2t}}{B_m} \quad (21)$$

$$B_m=\beta_m[(r^2l+kh)\sin(h\beta_m)\sin(rl\beta_m)-(rh+rkl)\cos(h\beta_m)\cos(rl\beta_m)] \quad (22)$$

where β_m's are positive roots of equation (23).

$$\sin(h\beta)\cos(rl\beta)+\frac{k}{r}\cot(h\beta)\sin(rl\beta)=0 \quad (23)$$

Methods

Three-dimensional graphic display was carried out by the use of the FORTRAN program of Mori[4] with a digital computer (DEC, PDP-11/03) and an XY-plotter (Watanabe, WX-4631). Other calculations were performed with a desktop computer (Hewlett-Packard, HP-85).

Results and Discussion

Drift of the Interface Concentration

For the parameter values of Table I, equations (20) and (22) are reduced to equation (24) and equation (23) becomes equation (25).

$$C_1(x=0)=0.6+2\sum_{m=1}^{\infty}\frac{e^{-\beta_m^2(D_1t)}}{\beta_m[1.75\tan(1.5\beta_m)-1.25\cos(0.5\beta_m)]} \quad (24)$$

$$3\sin(2\beta)=\sin(\beta) \quad (25)$$

Therefore, β_m's are evaluated by equation (26).

$$\left.\begin{aligned}\beta_{4n+1}&=2n\pi+\varphi\\ \beta_{4n+2}&=2n\pi+\pi\\ \beta_{4n+3}&=2n\pi+2\pi-\phi\\ \beta_{4n+4}&=2n\pi+2\pi\end{aligned}\right\} n=0,1,2,,,,\infty \quad (26)$$

where ϕ is the smallest positive root of equation (25) or 1.40334824758 radian. Numerical values of equation (24) were obtained with the program shown in Fig. 2. The computer output (Fig. 3) clearly shows that the interface concentration drifts from the value of (5) to that of (6).

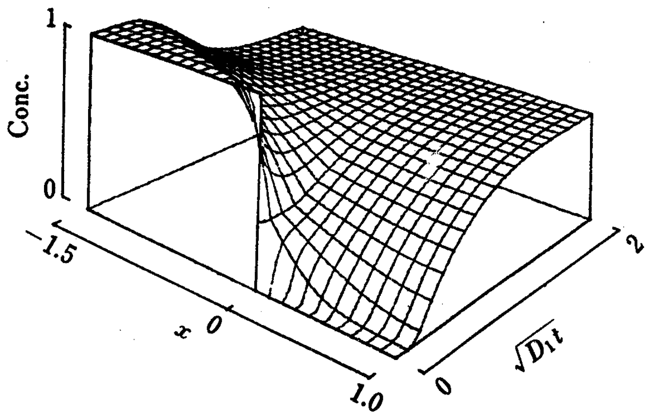

Fig. 4. Three–Dimensional Display of Diffusion Time Course

TABLE I. Parameter Values used for Calculation

k	1.0
r	0.5
h	1.5
l	1.0
C_0	1.0

Display of Diffusion Time Course

The diffusion time course of a finite composite system with the parameter values of Table I was calculated by means of equations (21) through (23) and is displayed three-dimensionally in Fig. 4, which visually shows momentary change of the concentration distribution, from the initial condition to final equilibrium.

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