

Carbon Tetrachloride Absorption in L-O-W-Density Polyethylene Pellets: Mathematical Analysis of Concentration Profiles

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Synopsis

Concentration profiles of carbon tetrachloride in low-density polyethylene pellets were analyzed mathematically to estimate the concentration dependence of the diffusivity. Profiles were measured by electron microprobe analysis and energy dispersive x-ray spectroscopy (EDAX) and found to be sharper than expected. However, the diffusion front position was proportional to \sqrt{t} rather than t as might have been expected if case II diffusion applied. The mathematical model assumed a constant diffusivity behind the diffusion front and zero diffusivity in advance of the front. The resulting moving boundary problem was solved by integral methods, yielding concentration profiles consistent with the essential features of the experimental profiles. The difference in shape between experimental and calculated profiles was attributed to the concentration dependence of the diffusivity, which was estimated by a curve-fitting procedure. The resulting integral average diffusivity was 1.28×10^{-6} cm²/s, four times that estimated assuming standard fickian absorption from the mass uptake curves. This difference was attributed to the inapplicability of the standard relationships to this system in which a discontinuous diffusivity concentration relationship was presumed to apply.

INTRODUCTION

Many investigators¹⁻⁴ have observed that a sharp moving boundary may result when a low-molecular-weight substance diffuses in a polymer. This may arise when the penetrant interacts with the medium to become immobilized (e.g., by reaction or adsorption) or when the diffusion coefficient is a discontinuous function of concentration. The latter situation is an example of an extreme type of concentration dependence that modifies the course of diffusion.

As part of a study into the relationship among extrusion processing conditions, polymer morphology, and the diffusion or migration of relatively large, slow penetrants, carbon tetrachloride vapor absorption in low-density polyethylene rods was measured using electron probe microanalysis.⁵ Carbon tetrachloride was considered to be a model penetrant whose chlorine atoms could be detected by energy dispersive x-ray spectroscopy. In these experiments, a sharp moving boundary was observed to separate a region in which the rod was saturated with CCl₄ from a region with no detectable penetrant.⁵ The position of the sharp boundary and the amount of absorbed penetrant were both found to be proportional to \sqrt{t} rather than to t , as might be expected for case II transport.⁶ These sorption features were

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presumed to be the consequence of a discontinuity in the diffusion coefficient-concentration relationship, consistent with the hypothesis of Crank.⁷ It was presumed that below a certain critical penetrant concentration there was a large decrease in the diffusion coefficient. In advance of the diffusion front where the concentration was lower than the critical value, the diffusivity was effectively near zero. This prevented diffusion further into the medium until the concentration at the point exceeded the critical value. The net result was a sharpened diffusion front that had lost its leading edge (Fig. 1).

This paper presents a mathematical analysis of the experimentally determined concentration profiles of CCl_4 in low-density polyethylene (LDPE) rods. It is based on the assumption of fickian diffusion with constant diffusivity behind the front (where the concentration is greater than the critical value) and zero diffusivity in advance of the front. The mathematical model combines fickian diffusion with the boundary conditions associated with a sharp moving front, in contrast with the standard model for case II transport for which the front moves at constant velocity because diffusion is relaxation controlled.

Integral methods were used to solve the relevant equations in an iterative fashion with the assumption of constant diffusivity. As explained below, the solution was then used in a curve-fitting procedure to estimate the concentration dependence of the CCl_4 -LDPE diffusion process. Integral methods^{8,9} involve postulating a concentration profile behind the moving boundary, although not necessarily the steady-state one. It usually takes the form of a polynomial that is made to satisfy all the boundary conditions and that also satisfies an integrated form of the diffusion equation. The position of the moving boundary emerges as the solution of an ordinary differential equation with time as the independent variable.

MATHEMATICAL MODEL

For radial diffusion only (a cylinder with ends capped), penetrant concentration C is a function of radius r and time t :

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(rD \frac{\partial C}{\partial r} \right) \quad (1)$$

where r is the radial distance measured from the center of the cylinder, and D is the diffusion coefficient, a function of C , in which a discontinuity occurs at a certain value of concentration (C_R).

The sharpness of the experimentally observed CCl_4 diffusion front, particularly at low concentration, makes it possible to introduce some simplifying assumptions. As far as the concentration profile and the overall rate of mass uptake are concerned, the concentration-dependent diffusion process resulting in a sharp moving boundary of concern here is identical to the moving boundary problem associated with immobilization of a penetrant with a constant diffusivity.^{10,11} Therefore the discontinuity was assumed to occur at $C_R = 0$, which at any time t is at a position $r = R(t)$, as shown

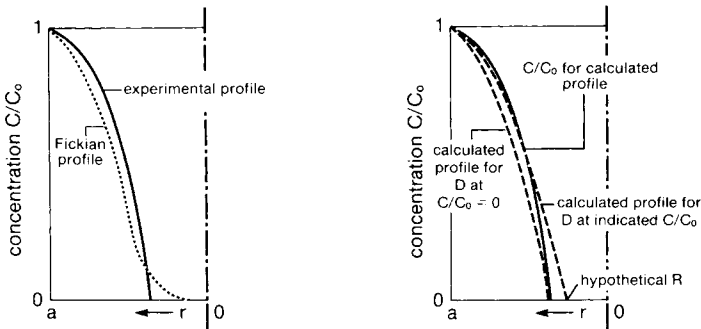


Fig. 1. Schematic illustration of concentration profiles of CCl₄ absorption in low-density polyethylene: (—) experimental profile; (---) calculated profile, with a constant diffusivity and a sharp moving boundary model; (···) typical fickian profile.

in Fig. 1. Then at time t the concentration in the region $R \leq r \leq a$ is denoted by $C(r, t)$ where a is the radius of the cylinder, and in the region $r \leq R$, by $C = 0$. A steep but continuous concentration-dependent diffusivity could have been used to describe the more realistic profile for $0 \leq C \leq C_R$. However, this would have made the equations more complex than necessary and correspondingly more difficult to solve.

The diffusivity is assumed constant, and a mass balance at the sharp moving boundary ($r = R$) yields

$$D \left(\frac{\partial C}{\partial r} \right)_{r=R} = -b \left(\frac{dR}{dt} \right) \quad (2)$$

The left-hand side of eq. (2) gives the flux at the moving boundary, which must be equal to the amount of penetrant behind the diffusion front; b is the capacity of the solid as limited by the solubility of the penetrant in the medium, and assuming a constant equilibrium surface concentration (C_0), $b = C_0$. A constant diffusivity has been assumed since formal treatment of the problem becomes intractable with a variable diffusion coefficient. The remaining boundary conditions are

$$C(a, t) = C_0 \quad t \geq 0 \quad (3)$$

$$C(r, 0) = 0 \quad t = 0 \quad (4)$$

Equation (1), subject to the boundary conditions (2), (3), and (4), defines the moving boundary diffusion problem in a cylindrical medium.

Equation (1) was solved in an iterative fashion by the integral method, as detailed in the Appendix. The moving boundary diffusion equations were transformed from cylindrical to planar coordinates using a transformation similar to that used by Shih and Tsay.¹² The first-order approximation solution, in terms of the original variables, is given by (see Appendix)

$$t = \frac{ba^2}{4DC_0} \left\{ 1 + \left(\frac{R}{a} \right)^2 \left[\ln \left(\frac{R}{a} \right)^2 - 1 \right] \right\} \quad (\text{A.21})$$

$$\frac{C}{C_0} = \frac{\ln(R/r)}{\ln(R/a)} \quad (\text{A.22})$$

which are the same as those of a pseudo-steady-state solution.¹³ The first-order approximation concentration profile [eq. (A.20)] was assumed behind the moving boundary and used to obtain the second-order approximation [eq. (A.23)], which was in turn used to generate the third-order approximation [eq. (A.29)]. In theory, the iteration procedure could be repeated indefinitely, but the complexity of higher order approximations makes them too difficult to obtain.

CCl₄/LDPE CONCENTRATION PROFILES

Concentration profiles of CCl₄ diffusing into low-density polyethylene rods at 40°C at various absorption times (Fig. 2) were measured by electron microprobe analysis using energy dispersive x-ray spectroscopy (EDAX), as explained in the preceding paper,⁵ without the need for calibration. Briefly, LDPE resin pellets as supplied by the manufacturer (CIL 300 GXN 7218) were exposed to pure carbon tetrachloride vapor at 40°C in a sorption apparatus. The ends of the pellets were capped so that only radial diffusion would occur. After various predetermined times, samples were removed from the sorption chamber and stored on dry ice. To prepare the sample for EDAX analysis, the pellet was cut smoothly perpendicular to its axis, coated with a thin layer of carbon, and placed on a carbon block in a scanning electron microscope (ISI-60, Hitachi, Japan). The sample was scanned across its diameter in 60 s in the line profile mode with the intensity of the x-rays corresponding to chlorine atoms analyzed and recorded on photographic film (γ -PGT-1000, Princeton Gamma-Tech., Princeton, New Jersey). The total time in sample preparation operations was approximately 5–7 min. The negligible effect of this on the concentration profile was discussed in the previous paper.⁵

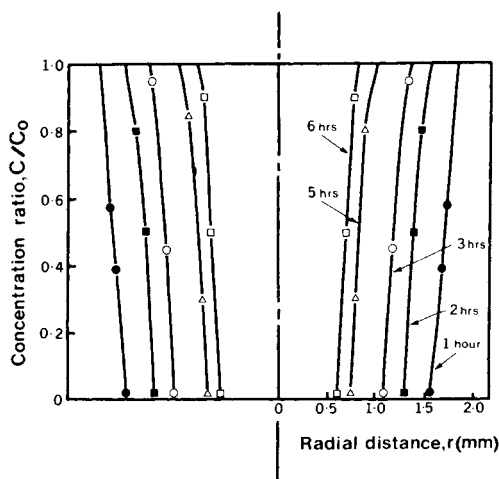


Fig. 2. Experimental concentration profiles for CCl₄ in low-density polyethylene pellets at 40°C as measured by EDAX.⁵

Average values of diffusivity were calculated from the first-, second-, and third-order approximations. The position of the front at $C/C_0 = 0$ measured from the center of the cylinder at each absorption time was used in eq. (A.3) to get the positions of the fronts in transformed coordinates (x). The corresponding values of τ were calculated from eq. (A.19) (first-order approximation), eq. (A.23) (second-order approximation), or eq. (A.29) (third-order approximation), ultimately to yield the average diffusivity. Since the shapes of the experimental concentration profiles indicated that the equilibrium concentration could be assumed equal to the surface concentration, α (the ratio of surface to equilibrium concentration) in these equations was taken equal to unity.

The concentration dependence of the diffusivity was estimated by a curve-fitting procedure illustrated in Fig. 1. For each concentration profile, the radial distance was measured for a particular C/C_0 value. This value of radial distance was used in eq. (A.22) (first-order approximation) to obtain the corresponding position of the front at $C/C_0 = 0$ as if the diffusivity at the nonzero C/C_0 position had applied over the entire moving front. The resulting hypothetical position of the front was then used in eq. (A.21) to estimate the diffusivity that would correspond to the chosen ($r, C/C_0$) and hypothetical ($R, 0$). This procedure was repeated with each of the five experimental concentration profiles at various values of C/C_0 to obtain five estimates of the diffusivity for each C/C_0 value.

RESULTS

As shown in Table I, the values of average diffusivity obtained from the five front positions (Fig. 2) provided quite consistent values. The average value of diffusivity obtained from the first-order approximation was about 30% lower than that obtained from the second-order solution, indicating the need for higher order approximations (Table I). The value of diffusivity from the second-order approximation was only about 4.7% lower than the

TABLE I
Diffusivity of Carbon Tetrachloride in LDPE Pellets at 40°C^a

Time t (h)	Distance from axis of cylinder to front at $C/C_0 = 0, R$ (cm)	Diffusivity (third-order approximation) ($\times 10^{-7}$ cm ² /s)
1	0.160	6.57
2	0.132	6.86
3	0.110	6.99
5	0.075	6.69
6	0.061	6.54
Mean \pm SD		6.77 ± 0.20

Calculated from R using eqs. (A.29), (A.30), and (A.31).

^a Estimated from the concentration profile at $C/C_0 = 0$. First-order approximation: $4.48 \times 10^{-7} \pm 0.23 \times 10^{-7}$ cm²/s; 30.1% lower than second-order approximation. Second-order approximation: $6.41 \times 10^{-7} \pm 0.18 \times 10^{-7}$ cm²/s; 4.8% lower than third-order approximation.

value of diffusivity obtained from the third-order approximation. Thus the contribution of the third-order approximation was quite low, and the more difficult to obtain higher order approximations were unnecessary.

Diffusivity values as a function of concentration estimated by the curve-fitting procedure from the experimental concentration profile (corresponding to 1 h of CCl_4 absorption) are shown in Table II. The resulting diffusivities obtained from five concentration profiles were averaged and plotted against relative concentration (C/C_0) in Fig. 3. The semilogarithmic plot was used to determine the constants in the standard equation for a concentration-dependent diffusivity $D = D_0 \exp(\beta C/C_0)$: $\beta = 1.627$ and $D_0 = 4.1 \times 10^{-7} \text{ cm}^2/\text{s}$. These values of β and D_0 were used to calculate the integral average diffusivity: $1.28 \times 10^{-6} \text{ cm}^2/\text{s}$. This value was corrected for the difference between first- and third-order approximations by multiplying by 1.34 (as per the difference between first- and third-order approximations given in Table I). The resulting estimate, $1.9 \times 10^{-6} \text{ cm}^2/\text{s}$, is still almost four times that determined from the conjugate sorption curves assuming Fick's law (4.5×10^{-7}). This plot does not show the maximum expected from the crossover of absorption and desorption mass uptake curves seen in an earlier microbalance study.¹⁴

Diffusivity estimates at each C/C_0 value were found to decrease progressively from the $t = 1 \text{ h}$ to $t = 5 \text{ h}$ profiles; accordingly, the range of values and midpoint are shown on Fig. 3 rather than the average and standard deviation. This range was particularly wide at $C/C_0 = 0.9$.

DISCUSSION

The sharp moving boundary manifested in the concentration profiles of CCl_4 in LDPE rods⁵ suggested that the diffusion behavior was influenced by a limited case of concentration-dependent diffusion with a discontinuity in the diffusivity-concentration relationship at low concentration. Because of this sharp boundary phenomenon, the use of a fickian diffusion model was not considered valid for estimating the diffusivity in this system. Consequently, an unsteady-state semianalytic model was developed to incor-

TABLE II
Concentration-Dependent Diffusivities for Carbon Tetrachloride in Low-Density Polyethylene Pellets at 40°C^a

Time <i>t</i> (h)	Concentration C/C_0	Radial distance	Hypothetical position	Diffusivity <i>D</i> ($\times 10^{-7} \text{ cm}^2/\text{s}$) ^c
		from concentration profiles <i>r</i> (cm)	of front at $C/C_0 = 0^*$ <i>R</i> (cm) ^b	
1	0.1	0.162	0.157	5.16
	0.3	0.166	0.147	6.77
	0.5	0.175	0.138	8.25
	0.7	0.180	0.118	13.5
	0.9	0.186	0.038	29.4

^a Estimated from 1-h concentration profile by a curve-fitting procedure.

^b Calculated from *r* using eq. (A.22).

^c Calculated from *R* using eq. (A.21).

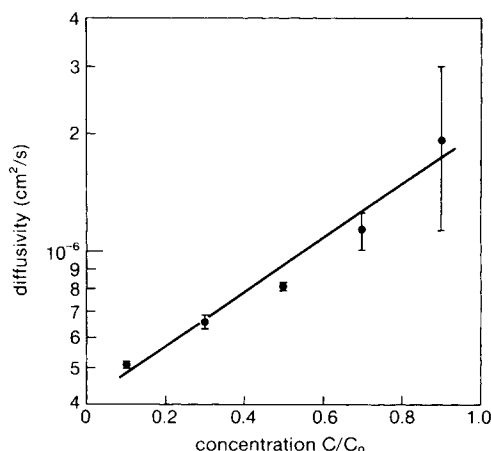


Fig. 3. Concentration-dependent diffusion coefficients estimated from concentration profiles at each C/C_0 using curve-fitting procedure. Range of values and midpoint shown for each C/C_0 value.

porate the boundary conditions for a sharp moving front into the diffusion process. This diffusion model with a sharp boundary assumed the diffusion coefficient to be constant along and behind the boundary (except at $C/C_0 = 0$), since formal mathematical treatment of the diffusion equation became too difficult when a variable diffusion coefficient was involved. The assumption of a constant diffusivity seemed to be a reasonable first step for developing the model with a moving boundary. Crank^{10,11} reported that if diffusion is characterized by a constant diffusion coefficient, the diffusion and immobilization process with a sharp moving boundary resembles, as far as the distribution of total concentration and overall rate of uptake are concerned, the more complex concentration-dependent diffusion process.

The apparent discontinuity in CCl_4 diffusivity at low concentration was presumed to reflect the role of swelling and plasticization in determining the rate of absorption. Behind the advancing diffusion front, the polymer is swollen by the absorbed CCl_4 , increasing its diffusivity; in advance of the front the concentration is near zero and the CCl_4 must diffuse through unswollen polymer at what is presumed to be a very low rate. The unswollen amorphous regions of LDPE are not glassy at 40°C , so that transport is not limited by the rate of relaxation in advance of the front and case II transport is not observed. Rather an intermediate level of behavior is apparent: fickian diffusion behind the front that moves in proportion to the \sqrt{t} rather than in proportion to t .

The value of $\alpha (= C_0/b)$ in this model was taken as unity since the surface concentration (C_0) was assumed to be equal to the equilibrium saturation (i.e., the saturation capacity of the medium, b). This relatively high value of α made the contribution of the second approximation 30%, as shown in Table I.

The difference between the experimental concentration profiles obtained by the EDAX technique and the profiles generated using the mathematical model, assuming a constant diffusivity, was used to study the dependence of diffusivity on concentration in the CCl_4 -LDPE system. The estimated

diffusivity increased with an increase of concentration. However, the presence of a distinct maximum in the diffusivity-concentration relationship at a near saturation value of concentration (the mass uptake curves intersected at $M_t/M_\infty = 0.95$) could not be seen. The dependence of diffusivity on concentration between $C/C_0 = 0.9$ and 1.0 could not be evaluated from the concentration profiles since it was difficult to determine precisely the shape of the concentration profiles in this narrow range of concentration, near equilibrium. Confirmation of the validity of the EDAX technique and the mathematical analysis must await further experiments with CCl_4 diffusion at higher temperatures for which the expected maximum in diffusivity (corresponding to the point of intersection of absorption and desorption curves) would be at lower values of C/C_0 . The maximum in the diffusivity-concentration relationship at lower values of C/C_0 was attributed to clustering of CCl_4 , which at higher temperatures and corresponding vapor activities would occur at lower values of C/C_0 .¹⁴

The discontinuity in the diffusivity concentration relationship at a low value of concentration was also not seen in Fig. 3. This was presumed to be due to the very low value of concentration at which this discontinuity was expected to arise. At such low concentration (less than $C/C_0 = 0.1$) it was not possible to determine precisely the experimental concentration profiles.

Although the integral value of diffusivity estimated from concentration profiles was almost four times that determined from the conjugate sorption curves assuming Fick's law, this comparison was not considered reasonable. The presence of the sharp moving boundary (and the discontinuity in the diffusivity-concentration relationship) negated assumptions inherent to the fickian absorption process and invalidated the calculation based on conjugate sorption kinetics. The EDAX technique, most significantly, indicated that CCl_4 -LDPE diffusion occurred with a sharp moving boundary although further refinements to the technique are necessary to eliminate topographical variations.¹⁴ Thus the integral diffusivity values obtained from the concentration profiles may be sensitive to the method of measurement. However, this effect is believed to be small because of the reasonably good agreement between the mass uptake values obtained by EDAX and the standard sorption technique.¹²

CONCLUSIONS

Concentration profiles of carbon tetrachloride in low-density polyethylene pellets were analyzed mathematically by a moving boundary model that assumed a constant diffusivity behind the observed sharp diffusion front and zero diffusivity in advance of the front. The relevant equations were solved in an iterative fashion by integral methods, and the resulting equations yielded concentration profiles consistent with the essential features of the experimentally determined ones: front movement proportional to \sqrt{t} . The difference in shape between experimental and calculated profiles was attributed to the concentration dependence of the diffusivity. A reasonable relationship between diffusivity and concentration was estimated by a curve-fitting procedure that tended to substantiate the validity of the mathematical analysis. However, the analysis must be applied to other

profiles determined at different temperatures and for different systems before its general utility can be assessed.

APPENDIX

The moving boundary problem expressed in eqs. (1) through (4) was transformed from cylindrical to rectangular coordinates by a transformation similar to that of Shih and Tsay¹¹:

$$U = \frac{C}{C_0} \quad (\text{A.1})$$

$$x = \ln \frac{a}{r} \quad (\text{A.2})$$

$$X = \ln \frac{a}{R} \quad (\text{A.3})$$

$$\tau = \frac{tDC_0}{a^2b} \quad (\text{A.4})$$

$$\alpha = \frac{C_0}{b} \quad (\text{A.5})$$

Equations (1), (2), (3), and (4) then become

$$\alpha e^{-2x} \frac{\partial U}{\partial t} = \frac{\partial^2 U}{\partial x^2} \quad 0 \leq x \leq X(t) \quad (\text{A.6})$$

$$\frac{dX}{d\tau} = -\frac{1}{e^{-2X}} \left(\frac{\partial U}{\partial x} \right)_{x=X} \quad (\text{A.7})$$

$$U(0, \tau) = 1 \quad \tau \geq 0 \quad (\text{A.8})$$

$$U(X, 0) = 0 \quad t \geq 0 \quad (\text{A.9})$$

Integrating eq. (A.6) from any position X to the position of the moving front X , followed by substitution of (A.7), results in

$$\left(\frac{\partial U}{\partial x} \right)_x = -e^{-2X} \frac{dX}{d\tau} - \alpha \int_x^X e^{-2\xi} \frac{\partial U(\xi, \tau)}{\partial \tau} d\xi \quad (\text{A.10})$$

where ξ is a dummy variable. Equation (A.10) is integrated from $x = 0$ to x , and after substituting, the surface concentration $U(0, \tau) = 1$ [eq. (A.8)] and changing the time variable τ to position variable $X(\tau)$ yields

$$U(x, X) = 1 - xe^{-2X} \frac{dX}{d\tau} - \alpha \frac{\partial}{\partial \tau} \left(\int_0^x \int_\eta^X e^{-2\xi} U(\xi, X) d\xi d\eta \right) \quad (\text{A.11})$$

where η is a second dummy variable.

Changing the order of the integration of the second term in the bracket of expression (A.11) gives

$$\int_0^x \int_\eta^X e^{-2\xi} U(\xi, X) d\xi d\eta = \int_0^x \xi e^{-2\xi} U(\xi, X) d\xi + x \int_x^X e^{-2\xi} U(\xi, X) d\xi \quad (\text{A.12})$$

$$= I(x, X)$$

thereby defining $I(x, X)$.

Equation (A.11) becomes

$$U(x, X) = 1 - \left(X e^{-2X} + \alpha \frac{\partial I}{\partial X} \right) \frac{dX}{d\tau} \quad (\text{A.13})$$

since

$$\frac{\partial I}{\partial \tau} = \frac{\partial I}{\partial X} \frac{dX}{d\tau} \quad (\text{A.14})$$

Letting $x = X$ in the above expression, and since the concentration at the moving front is zero, that is, $U(x = X, X) = 0$, results in

$$\frac{d\tau}{dX} = X e^{-2X} + \alpha \frac{dG}{dX} \quad (\text{A.15})$$

where

$$G(X) = I(x = X, X) \quad (\text{A.16})$$

The relationship between τ and X is obtained after integrating eq. (A.15) and using the condition $x(0) = 0$:

$$\tau = \frac{1}{4} [1 - (1 + 2X)e^{-2X}] + \alpha G(X) \quad (\text{A.17})$$

It can be seen that τ is given in terms of X , the inverse of $X = X(\tau)$. $G(X)$ is a function of $U(x, X)$, which can be obtained by the substitution of eq. (A.15) into eq. (A.13):

$$U(x, X) = 1 - \frac{\left(x e^{-2X} + \alpha \frac{\partial I}{\partial X} \right)}{\left(X e^{-2X} + \alpha \frac{dG}{dX} \right)} \quad (\text{A.18})$$

Equations (A.17) and (A.18) can be solved by iteration. By first assuming

$\alpha = 0$, the terms containing $I(x, X)$ and $G(X)$ in eqs. (A.17) and (A.18) vanish, giving

$$\tau_I = \frac{1}{4} [1 - (1 + 2X)e^{-2X}] \tag{A.19}$$

$$U_I(x, X) = \frac{X - x}{X} \tag{A.20}$$

The subscript I here denotes the first-order approximation solution. Transforming back into cylindrical coordinates using eqs. (A.2), (A.3), and (A.4) yields

$$t = \frac{ba^2}{4DC_0} \left\{ 1 = \left(\frac{R}{a}\right)^2 \left[\ln \left(\frac{R}{a}\right)^2 - 1 \right] \right\} \tag{A.21}$$

$$\frac{C}{C_0} = \frac{\ln R/r}{\ln R/a} \tag{A.22}$$

Equations (A.21) and (A.22) are identical to the pseudo-steady-state solution.¹³

Now the first-order approximation concentration profile [eq. (A.20)] is assumed behind the moving boundary and is used to obtain an unsteady-state solution designed as a second-order approximation. Substitution of eq. (A.20) into eq. (A.12) and using $G(X) = I(x = X, X)$, one can evaluate $I_I(x, X)$, $G_I(X)$, $(\partial I_I(x, X)/\partial X)$ and $(XG_I(X)/dX)$.

With a nonzero α , eq. (A.17) can be written as

$$\tau_{II} = \tau_I + \alpha G_I(x) \tag{A.23}$$

where

$$G_I(X) = \frac{e^{-2X}}{4X} (1 + X) + \frac{1}{4x} (X - 1) \tag{A.24}$$

and eq. (A.18) becomes

$$U_{II}(x, X) = 1 - \frac{(xe^{-2X} + \alpha \partial I_I/\partial X)}{(Xe^{-2X} + \alpha dG_I/dX)} \tag{A.25}$$

where

$$\frac{\partial I_I}{\partial X} = -\frac{xe^{-2x}}{4X^2} - \frac{e^{-2X}}{4X^2} + \frac{1}{4X^2} - \frac{xe^{-2X}}{2X} - \frac{xe^{-2X}}{4X^2} \tag{A.26}$$

The relationship between τ and X and the concentration profile are obtained by substitution of (A.24) and (A.23) and also (A.26) into (A.25).

$$\tau_{II} = \frac{1}{4} [1 - (1 + 2X)e^{-2X}] + \alpha \left[\frac{e^{-2X}}{4X} (1 + X) + \frac{1}{4X} (X - 1) \right] \tag{A.27}$$

$$U_{II} = 1 - \frac{\left[xe^{-2X} + \alpha \left(-\frac{xe^{2x}}{4^2} - \frac{e^{-2x}}{4X^2} + \frac{1}{4x^2} - \frac{xe^{-2X}}{2X} - \frac{xe^{-2X}}{4X^2} \right) \right]}{\left[Xe^{-X} + \alpha \left[-\frac{e^{-2X}}{2X} - \frac{e^{-2X}}{4X^2} - \frac{e^{-2X}}{2} + \frac{1}{4X^2} \right] \right]} \quad (\text{A.28})$$

Again, substitution of eq. (A.28) into eq. (A.12) and using ($G(X) = I(x = X, X)$) results in a third-order approximation to the unsteady-state solution. This is

$$\tau_{III} = \tau_I + \alpha G_{II}(X) \quad (\text{A.29})$$

where

$$\begin{aligned} G_{II}(X) = & \left[\frac{e^{-2X}}{-2} \left(X + \frac{1}{2} \right) + \frac{1}{4} \right] + \frac{e^{-2X}}{2Q} \left[e^{-2X} \left(X^2 + X + \frac{1}{2} \right) - \frac{1}{2} \right] \\ & + \frac{\alpha}{4X^2Q} \left[\frac{e^{-4X}}{-4} \left(X^2 + \frac{X}{2} + \frac{1}{8} \right) + \frac{1}{32} \right] \\ & + \frac{\alpha}{4X^2Q} \left[\frac{e^{-4X}}{-4} \left(X + \frac{1}{4} \right) + \frac{1}{16} \right] \end{aligned} \quad (\text{A.30})$$

$$\begin{aligned} & + \frac{\alpha}{4X^2Q} \left[\frac{e^{-2X}}{2} \left(X + \frac{1}{2} \right) - \frac{1}{4} \right] \\ & + \frac{\alpha e^{-2X}}{2XQ} \left[\frac{e^{-2X}}{-2} \left(X^2 + X + \frac{1}{2} \right) + \frac{1}{4} \right] \\ & + \frac{\alpha e^{-2X}}{4X^2Q} \left[\frac{e^{-2X}}{-2} \left(X^2 + X + \frac{1}{2} \right) + \frac{1}{2} \right] \\ Q = & \left[Xe^{-2X} + \left(-\frac{e^{-2X}}{2X} - \frac{e^{-2X}}{4X^2} - \frac{e^{-2X}}{2} + \frac{1}{4X^2} \right) \right] \end{aligned} \quad (\text{A.31})$$

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