

Dissolution of Solid Particles in Liquids: A Shrinking Core Model

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Abstract—The dissolution of spherical particles in liquids is analyzed dynamically. Here, we consider the case the dissolution of solute yields a solute-free solid phase in the outer portion of a particle. As dissolution proceeds, the interface between the undissolved solid phase and the solute-free solid phase moves towards the center of the particle. We assume that there exist two resistances for the diffusion of solute molecules: the resistance due to the solute-free portion of the particle and that due to a surface layer near solid-liquid interface. In general, the equation governing the dynamic behavior of dissolution needs to be solved numerically. However, analytical expressions for the temporal variation of the size of the undissolved portion of a particle and the variation of dissolution time can be obtained in some special cases. The present analysis takes the effect of variable bulk solute concentration on dissolution into account.

Keywords—dissolution of particles, surface layer, shrinking core model, dissolution time.

I. INTRODUCTION

THE dissolution of solid particles in liquids can roughly be described by two process in series: the escape of solute molecules from the solid surface and the diffusion of these molecules toward the bulk liquid phase. Depending on the operating condition, the rate of dissolution may be controlled by one of these two steps [1],[2]. A model often used for the description of the transport of solute molecules to the bulk liquid phase is the film theory proposed by Sherwood et al [3]. This approach provides a convenient way of describing the dynamic phenomenon under consideration. However, since the concentration of solute in the bulk liquid phase is assumed constant, it is most appropriate for the case of low solubility. By assuming that the bulk liquid phase is stagnant and of infinite size, Chen and Wang [4] have derived an analytical expression for the variation of dissolution time as a function of the concentration of solute in the bulk liquid phase. For the dissolution of particles comprise inorganic and electrochemical materials, the method of invariant functions is often adopted for the description of its dissolution kinetics [5].

In some cases, the solubility of only one of the components contained in the solid phase is appreciable compared with the rest components. In these cases, if the amount of the dissolving component is limited, the appearance of the solid phase will

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remain essentially unchanged during the course of dissolution. As dissolution proceeds, the undissolvable solid phase provides a resistance for the diffusion of solute molecules toward the bulk liquid phase. This can be advantageous in practical applications. A well-known example is the controlled-release of an active agent in drug [6] and fertilizer [7] where the resistance due to the undissolvable solid is utilized to maintain the dissolution rate on a certain favorable level.

The purpose of this report is to examine the dynamic behavior of the dissolution of solid particles in liquids. In particular, we are interested in the case the dissolution yields a solute-free solid phase. An attempt is made to take the effect of finite bulk liquid on dissolution into account. The mathematical representation thus obtained us not limited to the magnitude of solubility.

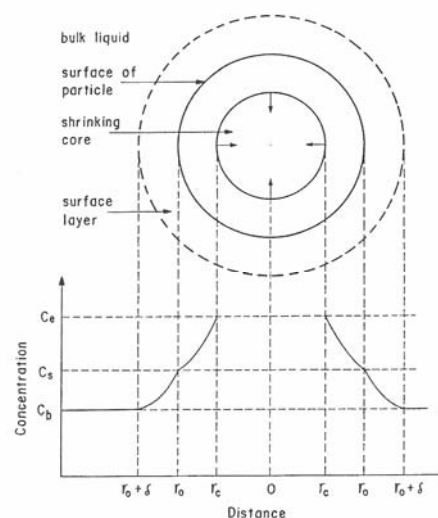


Fig. 1 A schematic representation of the dissolution phenomenon under consideration

II. ANALYSIS

By referring to Fig. 1, we assume that there exists a surface layer near the surface of a spherical particle. Also, the dissolution of solute yields a solute-free solid phase on the outer portion of the particle. As dissolution proceeds, the interface between the undissolved solid phase and the solute-free solid phase moves towards the center of the particle. The dissolution of solute consists of three steps in series: (i) Diffusion of solute molecules from the solid-solid interface through the solute-free portion of the particle to the solid-liquid

interface. (ii) Diffusion of solute molecules from the solid-liquid interface through the surface layer to the outer boundary of the surface layer. (iii) Diffusion of solute molecules from the outer boundary of the surface layer to bulk liquid phase. Suppose that the concentration of solute on the solid-liquid interface is at saturation. On the basis of these assumptions, a solute balance over the solute-free portion of the particle and the surface layer region yields, respectively,

$$\frac{\partial C}{\partial t} = \frac{D_1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial C}{\partial r}), \quad r_c < r < r_0 \quad (1)$$

$$\frac{\partial C}{\partial t} = \frac{D_2}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial C}{\partial r}), \quad r_0 < r < r_0 + \delta \quad (2)$$

where C denotes the concentration of solute, t is time, D_1 and D_2 are respectively, the effective diffusivity of solute in the solute-free solid phase and the diffusivity of solute in the surface layer, r_0 and r_c are, respectively, the radius of the particle and the radius of core, δ is the thickness of the surface layer, and r is the distance measured from the center of the particle. If the diffusion rate of solute is much greater than the rate of moving of the solid-liquid interface towards the center of the particle, a pseudo-steady state can be assumed. In this case, (1) and (2) reduce to, respectively,

$$D_1 \frac{\partial}{\partial r} (r^2 \frac{\partial C}{\partial r}) = 0, \quad r_c < r < r_0 \quad (3)$$

$$D_2 \frac{\partial}{\partial r} (r^2 \frac{\partial C}{\partial r}) = 0, \quad r_0 < r < r_0 + \delta \quad (4)$$

Integrating these two equations, subject to the conditions $C=C_e$ at $r=r_c$, $C=C_s$ at $r=r_0$, and $C=C_b$, at $r=r_0+\delta$, we obtain

$$\frac{\partial C}{\partial r} = -\frac{C_e - C_s}{r^2(1/r_c - 1/r_0)}, \quad r_c < r < r_0 \quad (5)$$

$$\frac{\partial C}{\partial r} = -\frac{C_s - C_b}{r^2[1/r_0 - 1/(r_0 + \delta)]}, \quad r_0 < r < r_0 + \delta \quad (6)$$

where C_e , C_s , and C_b represent the concentrations of solute at dissolving front, at the solid-liquid interface, and in the bulk liquid phase, respectively. At the solid-liquid interface, we have

$$SD_1 \frac{dC}{dr} \Big|_{r=r_0} = SD_2 \frac{dC}{dr} \Big|_{r=r_0} \quad (7)$$

where S denotes the surface area of the particle. By referring to (5) and (6), this expression becomes

$$D_1 \frac{C_e - C_s}{1/r_c - 1/r_0} = D_2 \frac{C_s - C_b}{1/r_0 - 1/(r_0 + \delta)} \quad (8)$$

Solving this expression for C_s , we obtain

$$C_s = \frac{\eta C_b / [1/r_0 - 1/(r_0 + \delta)] + C_e / (1/r_c - 1/r_0)}{\eta / [1/r_0 - 1/(r_0 + \delta)] + 1/(1/r_c - 1/r_0)} \quad (9)$$

where $\eta = D_2/D_1$. Let m be the number of moles of solute contained in the solid particle. At pseudo-steady state, we have

$$\frac{dm}{dt} = 4\pi r^2 D_1 \frac{dC}{dr} = \text{constant} \quad (10)$$

Integrating this equation with respect to r , subject to the boundary conditions $C=C_e$ at $r=r_c$ and $C=C_s$ at $r=r_0$, yields

$$(1/r_c - 1/r_0) \left(\frac{dm}{dt} \right) = -4\pi D_1 (C_e - C_s) \quad (11)$$

Substituting (9) into this expression and noting that $m = 4\pi r_c^3 \rho \varepsilon / 3M$, we have

$$\begin{aligned} r_c^2 \left[1 + \frac{\eta(1/r_c - 1/r_0)}{1/r_0 - 1/(r_0 + \delta)} \right] \left(\frac{dr_c}{dt} \right) \\ = \frac{-MD_1 \eta (C_e - C_b)}{\rho \varepsilon [1/r_0 - 1/(r_0 + \delta)]} \end{aligned} \quad (12)$$

where M denotes the molecular weight of solute, ρ is the density of particle, and ε is the weight fraction of solute.

A. Constant Bulk Concentration

If the volume of the bulk liquid phase V is large enough, the concentration of solute in the bulk liquid phase is essentially constant. Denote this concentration as C_0 . For convenience, (12) nondimensionlized as

$$[r_c^{*2} (P - \eta) + \eta r_c^*] \left(\frac{dr_c^*}{dt^*} \right) = -\eta C^* \quad (13)$$

where

$$C^* = 3VM(C_e - C_0) / 4\pi \rho r_0^3 \varepsilon n \quad (13a)$$

$$\delta^* = \delta / r_0 \quad (13b)$$

$$P = 1 - 1/(1 + \delta^*) \quad (13c)$$

$$r^* = r_c / r_0 \quad (13d)$$

$$t^* = 4\pi D_1 r_0 n / 3V \quad (13e)$$

where n is the number of particles. Solving (13), subject to the initial condition $r_c^* = 1$ at $t^* = 0$, we obtain

$$t^* = -\{[(r_c^{*3} - 1)(P - \eta) / 3] + [\eta(r_c^{*2} - 1) / 2]\} / \eta C^* \quad (14)$$

This equation describes implicitly the variation of the radius of a particle as a function of time.

B. Variable Bulk Concentration

If the volume of the bulk liquid phase is finite, the variation of the bulk liquid concentration is

$$\begin{aligned} C_b &= C_0 + \frac{4\pi\rho\varepsilon n(r_0^3 - r_c^3)}{3VM} - n\left(\int_{r_c}^{r_0+\delta} 4\pi r^2 C dr\right) / V \\ &= C_0 + \frac{4\pi\rho\varepsilon n(r_0^3 - r_c^3)}{3VM} \\ &\quad - n\left(\int_{r_c}^{r_0} 4\pi r^2 C dr + \int_{r_0}^{r_0+\delta} 4\pi r^2 C dr\right) / V \end{aligned} \quad (15)$$

The variation of C as a function of r at pseudo-steady state can be obtained by integrating (5) and (6) with the conditions $C=C_e$ at $r=r_c$, $C=C_s$ at $r=r_0$, and $C=C_b$ at $r=r_0+\delta$. The results are

$$C = -k_1/r + k_2, \quad r_c < r < r_0 \quad (16)$$

$$C = -k_1'/r + k_2', \quad r_0 < r < r_0 + \delta \quad (17)$$

where

$$k_1 = -(C_e - C_s) / (1/r_c - 1/r_0) \quad (17a)$$

$$k_2 = (C_s / r_c - C_e / r_0) / (1/r_c - 1/r_0) \quad (17b)$$

$$k_1' = -(C_s - C_b) / [1/r_0 - 1/(r_0 + \delta)] \quad (17c)$$

$$k_2' = [C_b / r_0 - C_s / (r_0 + \delta)] / [1/r_0 - 1/(r_0 + \delta)] \quad (17d)$$

Substituting (16) and (17) into (15), we obtain

$$\begin{aligned} C_b &= C_0 + \frac{4\pi\rho\varepsilon n(r_0^3 - r_c^3)}{3VM} \\ &\quad - 4\pi n \left\{ -\frac{k_1}{2}(r_0^2 - r_c^2) + \frac{k_2}{3}(r_0^3 - r_c^3) \right. \\ &\quad \left. - \frac{k_1'}{2}[(r_0 + \delta)^2 - r_0^2] + \frac{k_2'}{3}[(r_0 + \delta)^3 - r_0^3] \right\} / V \end{aligned} \quad (18)$$

Substituting C_s from (9) into (17a) through (17d) and substituting the resultant expressions into (18), we have

$$C_b = C_0 + \frac{4\pi n[\rho\varepsilon(r_0^3 - r_c^3) / 3M - f_2 C_e] / V}{1 + 4\pi n f_1 / V} \quad (19)$$

where

$$f_1 = -\frac{(r_0^2 - r_c^2)b_2}{2} + \frac{(r_0^3 - r_c^3)b_4}{3} - \frac{[(r_0 + \delta)^2 - r_0^2]b_6}{2} + \frac{[(r_0 + \delta)^3 - r_0^3]b_8}{3}$$

$$f_2 = -\frac{(r_0^2 - r_c^2)b_1}{2} + \frac{(r_0^3 - r_c^3)b_3}{3} - \frac{[(r_0 + \delta)^2 - r_0^2]b_5}{2} + \frac{[(r_0 + \delta)^3 - r_0^3]b_7}{3}$$

In these expression,

$$b_1 = -(1 - a_2) / (1/r_c - 1/r_0)$$

$$b_2 = a_1 / (1/r_c - 1/r_0)$$

$$b_3 = (a_2 / r_c - 1/r_0) / (1/r_c - 1/r_0)$$

$$b_4 = (a_1 / r_c) / (1/r_c - 1/r_0)$$

$$b_5 = -a_2 / [1/r_0 - 1/(r_0 + \delta)]$$

$$b_6 = (1 - a_1) / [1/r_0 - 1/(r_0 + \delta)]$$

$$b_7 = -[a_2 / (r_0 + \delta)] / [1/r_0 - 1/(r_0 + \delta)]$$

$$b_8 = [1/r_0 - a_1 / (r_0 + \delta)] / [1/r_0 - 1/(r_0 + \delta)]$$

where

$$a_1 = \frac{\eta / [1/r_0 - 1/(r_0 + \delta)]}{\eta / [1/r_0 - 1/(r_0 + \delta)] + 1 / (1/r_c - 1/r_0)}$$

$$a_2 = \frac{1 / (1/r_c - 1/r_0)}{\eta / [1/r_0 - 1/(r_0 + \delta)] + 1 / (1/r_c - 1/r_0)}$$

Substituting (19) into (12), gives

$$\begin{aligned} &[r_c^{*2}(P - \eta) + \eta r_c^*] \frac{dr_c^*}{dt} \\ &= -\eta \left[\frac{C^* - (1 - r_c^{*3}) + C_e^*(f_1^* + f_2^*)}{1 + f_1^* / V^*} \right] \end{aligned} \quad (20)$$

where

$$C_e^* = \frac{C_e}{\rho\varepsilon / 3M}$$

$$f_1^* = f_1 / r_0^3$$

$$f_2^* = f_2 / r_0^3$$

$$V^* = V / 4\pi r_0^3$$

Special cases

If $\delta / r_0 \ll 1$, then (15) reduces to

$$\begin{aligned} C_b &= C_0 + \frac{4\pi\rho\varepsilon n(r_0^3 - r_c^3)}{3VM} - n\left(\int_{r_c}^{r_0} 4\pi r^2 C dr\right) / V \\ &= C_0 + \frac{4\pi\rho\varepsilon n(r_0^3 - r_c^3)}{3VM} \\ &\quad - 4\pi n\left\{-\frac{k_1}{2}(r_0^2 - r_c^2) + \frac{k_2}{3}(r_0^3 - r_c^3)\right\} \end{aligned} \quad (21)$$

If $C_e \ll \rho\varepsilon / M$ and $\delta / r_0 \ll 1$, then

$$C_b = C_0 + \frac{4\pi\rho\varepsilon n(r_0^3 - r_c^3)}{3VM} \quad (22)$$

Substituting this expression into (12), we obtain, after simplification,

$$[r_c^{*2}(P - \eta) + \eta r_c^*] \frac{dr_c^*}{dt^*} = -\eta(r_c^{*3} - 1 + C^*) \quad (23)$$

Solving this equation, subject to the initial condition $r_c^* = 1$ at $t^* = 0$, we obtain

$$\begin{aligned} t^* &= -\{[(P - \eta) / 3] \ln[(r_c^{*3} + \alpha^3) / (1 + \alpha^3)] \\ &\quad + (\eta / 3\alpha) \{-\ln[(r_c^* + \alpha) / (1 + \alpha)] \\ &\quad + \ln[(r_c^* - \alpha / 2)^2 + 3\alpha^2 / 4] / ((1 - \alpha / 2)^2 + 3\alpha^2 / 4)\} / 2 \\ &\quad + \sqrt{3}[\tan^{-1}((2r_c^* - \alpha) / \sqrt{3}\alpha) \\ &\quad - \tan^{-1}((2 - \alpha) / \sqrt{3}\alpha)]\} / \eta \end{aligned} \quad (24)$$

where $\alpha^3 = C^* - 1$.

C. Dissolution Time

The dimensionless time required to dissolve a particle, or the dimensionless dissolution time, t_d^* , can be evaluated by letting $r_c^* = 0$ in either (14) or (24). We have, for the case of constant bulk concentration

$$t_d^* = [(P - \eta) / 3 + \eta / 2] / \eta C^* \quad (25)$$

and for the case of variable bulk concentration with $C_e \ll \rho\varepsilon / M$ and $\delta / r_0 \ll 1$

$$\begin{aligned} t_d^* &= -\{[(P - \eta) / 3] \ln[\alpha^3 / (1 + \alpha^3)] \\ &\quad + (\eta / 3\alpha) \{-\ln[\alpha / (1 + \alpha)] \\ &\quad + \ln[\alpha^2 / ((1 - \alpha / 2)^2 + 3\alpha^2 / 4)] / 2 \\ &\quad - \sqrt{3}[\tan^{-1}(\sqrt{3}) + \tan^{-1}((2 - \alpha) / \sqrt{3}\alpha)]\} / \eta \end{aligned} \quad (26)$$

D. Solid Phase Diffusion Control

If $\eta \gg 1$ (or $D_2 \gg D_1$), the diffusion resistance due to surface layer is negligible. By following the similar procedure as that employed for the derivation of (14) through (26), it can be shown that, for the case of constant bulk concentration,

$$t^* = [(1 - r_c^{*2}) / 2 - (1 - r_c^{*3}) / 3] / C^* \quad (27)$$

$$t_d^* = 1 / 6C^* \quad (28)$$

and

$$\begin{aligned} t^* &= \{\ln[(r_c^* + \alpha) / (1 + \alpha)] \\ &\quad - \ln[(r_c^* - \alpha / 2)^2 + 3\alpha^2 / 4] / ((1 - \alpha / 2)^2 \\ &\quad + 3\alpha^2 / 4)\} / 2 - \sqrt{3}[\tan^{-1}((2r_c^* - \alpha) / \sqrt{3}\alpha) \\ &\quad - \tan^{-1}((2 - \alpha) / \sqrt{3}\alpha)]\} / \eta \\ &\quad + \ln[(r_c^{*3} + \alpha^3) / (1 + \alpha^3)] / 3 \end{aligned} \quad (29)$$

$$\begin{aligned} t_d^* &= \{\ln \alpha / (1 + \alpha) \\ &\quad - \ln[\alpha^2 / ((1 - \alpha / 2)^2 + 3\alpha^2 / 4)] / 2 \\ &\quad - \sqrt{3}[\tan^{-1}(1 / \sqrt{3}) - \tan^{-1}((2 - \alpha) / \sqrt{3}\alpha)]\} / 3\alpha \\ &\quad + \ln[\alpha^3 / (1 + \alpha^3)] / 3 \end{aligned} \quad (30)$$

for the case of variable bulk concentration with $C_e \ll \rho\varepsilon / M$ and $\delta / r_0 \ll 1$.

E. Surface Layer Diffusion Control

The definition of η suggests that if $\eta \ll 1$ (or $D_2 \ll D_1$), the diffusion resistance is mainly due to surface layer. It can be shown that, for the case of constant bulk concentration,

$$t^{*'} = P(1 - r_c^{*3}) / 3C^* \quad (31)$$

$$t_d^{*'} = P / 3C^* \quad (32)$$

where $t^{*'} = 4\pi D_2 r_0 n / 3V$, and $t_d^{*'}$ is the dimensionless dissolution time. For the case of variable bulk concentration with $C_e \ll \rho\varepsilon / M$ and $\delta / r_0 \ll 1$, we have

$$t^{*'} = -P \ln[(r_c^{*3} + \alpha^3) / (1 + \alpha^3)] / 3 \quad (33)$$

$$t_d^{*'} = -P \ln[\alpha^3 / (1 + \alpha^3)] / 3 \quad (34)$$

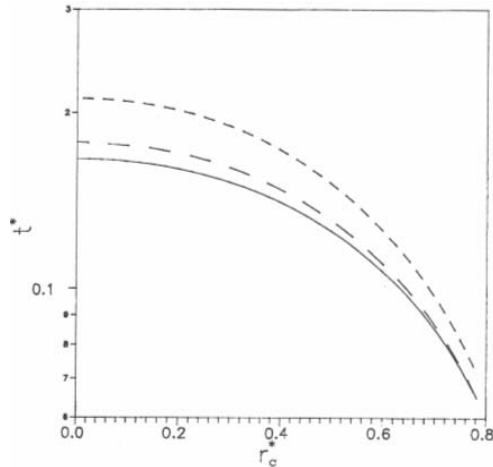


Fig. 2 Simulated temporal variation of the radius of the undissolved solid phase for the case $\delta^* = 0.1$, $V^* = 100$, $\eta = 0.5$, $C_0 = 0$, and $C^* = 3$.

Solid curve: constant bulk concentration, (14); long dash curve: variable bulk concentration with $C_e \ll \rho\epsilon/M$ and $\delta/r_0 \ll 1$, (23); short dash curve: variable bulk concentration, (20)

III. RESULTS AND DISCUSSION

Fig. 2 shows the simulated variation of the radius of the undissolved solid phase as a function of time. As can be seen from this figure, the dissolution is faster for the case of constant bulk liquid concentration than for the case of variable bulk liquid concentration. This is due to the decrease of concentration driving force during the course of dissolution for the latter. In a study of the controlled-release of progesterone from microcapsules, Gupta and Sparks [8] have derived a kinetic expression similar to (24). In their mathematical formulation, the solute distributed in the region $[r_c, r_0 + \delta]$ is neglected. As can be seen from Fig. 2, neglecting the solute contained in this region may lead to an appreciable error.

The variation of dissolution time as a function of concentration difference is shown in Fig. 3. As suggested by (13a), for a fixed solid-liquid combination, C^* increases with the increase of V . Thus, C^* is a measure of the relative significance of the variation of solute concentration in the bulk liquid phase. The greater the C^* , the less significant the variation of the solute concentration in the bulk liquid phase. Figure 3 reveals that if C^* is on the order of 10, the variation of the solute concentration in the bulk liquid phase is negligible. In other words, if $(C_e - C_0) > 40\pi r_0^3 \rho \epsilon n / 3VM$, the assumption of constant bulk concentration is appropriate in estimating the dissolution time of a particle. Note that the solute contained in the region $[r_c, r_0 + \delta]$ have a significant effect on dissolution time for small C^* .

The variation of dissolution time as a function of concentration different values of for the case $\delta^* = 0.3$ is shown in Fig. 4. As suggested by the definition of $\eta (= D_2 / D_1)$, if η is small, the dissolution is surface layer diffusion controlled-release, a specific material is often coated on the surface of a particle to reduce the rate of dissolution. Here, the coated solid plays the role of the surface layer of this study and D_2 is interpreted as the effective diffusivity of solute in the

coated material. The analysis is essentially the same as that presented in the present study.

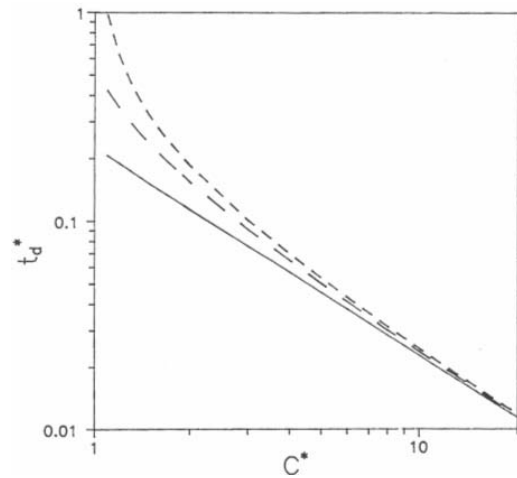


Fig. 3 Variation of dissolution time as a function of concentration difference. Solid curve: constant bulk concentration, (25); long dash curve: variable bulk concentration with $C_e \ll \rho\epsilon/M$ and $\delta/r_0 \ll 1$, (26); short dash curve: variable bulk concentration with $C_e \ll \rho\epsilon/M$ and $\delta/r_0 \ll 1$ not satisfied

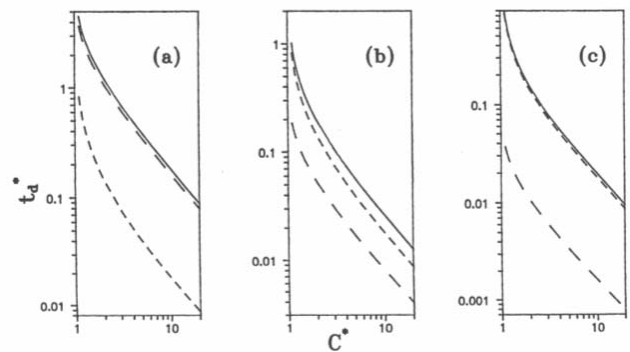


Fig. 4 Variation of dissolution time as a function of concentration difference for different values of for the case $\delta^* = 0.3$, $V^* = 100$, and $C_0 = 0$. Solid curve: (26); long dash curve: (30); short dash curve: (34). (a): $\eta = 0.05$; (b): $\eta = 1$; (c): $\eta = 5$

APPENDIX

If $\delta/r_0 \ll 1$, then

$$\int_{r_c}^{r_0+\delta} 4\pi r^2 C dr \cong \int_{r_c}^{r_0} 4\pi r^2 C dr \quad (A1)$$

Since $C < C_e$, we have

$$\int_{r_c}^{r_0} 4\pi r^2 C dr > \int_{r_c}^{r_0} 4\pi r^2 C_e dr = 4\pi C_e (r_0^3 - r_c^3) / 3 \quad (A2)$$

By referring to (15) in the text, we have

$$\begin{aligned} C_b &> C_0 + \frac{4\pi\rho\varepsilon n(r_0^3 - r_c^3)}{3VM} - \frac{4\pi m C_e(r_0^3 - r_c^3)}{3V} \\ &= C_0 + \frac{4\pi m(r_0^3 - r_c^3)}{3V} \left(\frac{\rho\varepsilon}{M} - C_e \right) \end{aligned} \quad (\text{A3})$$

Therefore if $C_e \ll \frac{\rho\varepsilon}{M}$,

$$C_b \cong C_0 + \frac{4\pi\rho\varepsilon n(r_0^3 - r_c^3)}{3VM} \quad (\text{A4})$$

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