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# TRANSIENT EFFECTS IN MASS TRANSFER TO CIRCULATING DROPS

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## NOMENCLATURE

| | |
|---|---|
| $B$, | dimensionless group defined by equation (14a); |
| $b$, | Chao's dimensionless group defined by equation (14b); |
| $\mathscr{D}_{Ac}, \mathscr{D}_{Ad}$, | effective pseudobinary diffusivity of solute $A$ in the continuous and dispersed phases respectively; |
| $j_A$, | radial component of the mass flux of solute $A$ relative to the mass-average velocity; |
| $K_d, k_d$, | instantaneous surface-mean mass-transfer coefficients defined by equations (4) and (5); |
| $m$, | slope of equilibrium distribution isotherm, $\mathrm{d}\rho_{Ad}/\mathrm{d}\rho_{Ac}$; |
| $R$, | sphere radius; |
| $S$, | surface area; |
| $t$, | time; |
| $V_\infty$, | approach velocity of continuous phase relative to sphere; |
| $x$, | $\cos\theta$. |

Greek symbols

| | |
|---|---|
| $\theta$, | angular co-ordinate in direction of interfacial fluid motion; |
| $\mu$, | viscosity; |
| $\rho$, | mass density; |
| $\rho_A$, | mass concentration of solute $A$; |
| $\tau$, | dimensionless time defined by equation (8). |

Subscripts

| | |
|---|---|
| $A$, | solute under consideration; |
| $c$, | continuous phase; |
| $d$, | dispersed phase; |
| $s$, | separation point; |
| $0$, | at interface; |
| $\infty$, | at large distance from interface. |

In a recent article by Ruckenstein [8], time-dependent solutions were obtained for the species continuity equation as applied to the boundary-layer of a circulating spherical drop. These solutions were based on the steady velocity profiles as obtained from the creeping flow and potential flow approximations of the Navier–Stokes equation. In applying the surface-stretch model [1] to similar situations, it has come to our attention that the expressions obtained by Ruckenstein are applicable only to limited situations and consequently must be used with great care. In particular, equation (37), Ref. [8], for the case in which the droplet phase resistance is controlling, does not give a useful description of the mass-transfer process except over a very restricted range of Péclet numbers. Also, equations (45) and (46), Ref. [8], are based on an unrealistic velocity profile in the interfacial region for moderate Reynolds numbers.

## THE SURFACE-STRETCH MODEL

An equivalent to equation (34), Ref. [8], may be obtained by using the generalized surface-stretch modification of the penetration theory [1] as applied to circulating drops. Application of the surface-stretch model gives the flux through the surface for an arbitrary surface element formed at time zero as:

$$j_A = (\rho_{A0} - \rho_{A\infty})_d \sqrt{\frac{\mathscr{D}_{Ad}}{\pi}} \frac{\left(\frac{\partial S}{\partial S_0}\right)_t}{\sqrt{\left[\int_0^t \left(\frac{\partial S}{\partial S_0}\right)_{t^*}^2 \mathrm{d}t^*\right]}} \tag{1}$$

where

$$\mathrm{d}S = 2\pi R^2 \sin\theta \, \mathrm{d}\theta \tag{2}$$

$$\mathrm{d}S_0 = 2\pi R^2 \sin\theta_0 \, \mathrm{d}\theta_0 \tag{3}$$

and $\theta_0$ and $\theta$ are the angular coordinates of an arbitrary ring-shaped surface element at times zero and $t$ respectively. The dispersed phase surface-average mass-transfer coefficient can be defined as:

$$\left(\frac{k_d}{\rho}\right)_{avg} = \frac{1}{4\pi R^2}\sqrt{\left(\frac{\mathscr{D}_{Ad}}{\pi}\right)} \int_{S_0} \frac{\left(\frac{\partial S}{\partial S_0}\right)_t^2 \mathrm{d}S_0}{\sqrt{\left[\int_0^t \left(\frac{\partial S}{\partial S_0}\right)_{t^*}^2 \mathrm{d}t^*\right]}}. \tag{4}$$

The relation corresponding to equation (4) for the continuous phase is identical in form and can be obtained simply by using the effective solute diffusivity in the continuous phase $\mathscr{D}_{Ac}$ in place of $\mathscr{D}_{Ad}$. Since the Whitman two-film theory holds when the penetration theory is valid [1] we may also define an overall mass-transfer coefficient

$$K_d = k_d \left[1 + m\sqrt{\left(\frac{\mathscr{D}_{Ad}}{\mathscr{D}_{Ac}}\right)}\right] \tag{5}$$

where $m$ is the slope of the equilibrium curve. Note that equation (5) defines a surface-mean instantaneous overall mass-transfer coefficient based on dispersed-phase concentration units. It will also be convenient to define a Sherwood number $Sh_d$ by

$$Sh_d = \frac{2RK_d}{\mathscr{D}_{Ad}}. \tag{6}$$

Explicit relations for $Sh_d$ can be obtained if the velocity profile is known.

## APPLICATION OF THE SURFACE-STRETCH MODEL UNDER CREEPING-FLOW CONDITIONS

We consider here a spherical drop in steady creeping flow through a quiescent external phase with the velocity distribution of Hadamard and Rybczynski. We assume the solute concentrations at zero time to be uniform within the drop and throughout the continuous phase. In addition we assume the surface-stretch modification of the penetration theory (1) to be applicable. We thus obtain (see Appendix):

$$Sh_d = \frac{2K_d R}{\mathscr{D}_{Ad}} \doteq \left\{\frac{192}{\pi}\frac{\mu_c}{\mu_c + \mu_d} Pe_d\right\}^{\frac{1}{2}} \times \left\{\frac{1}{1 + m\sqrt{(\mathscr{D}_{Ad}/\mathscr{D}_{Ac})}}\right\} I(\alpha\tau) \tag{7}$$

by application of equations (4)–(6). Here

$$Pe_d = \frac{2V_\infty R}{\mathscr{D}_{Ad}}; \qquad \alpha = \frac{Pe_d}{2}\frac{\mu_c}{\mu_c + \mu_d}; \qquad \tau = \frac{\mathscr{D}_{Ad}t}{R^2} \tag{8}$$

and

$$I(\alpha\tau) = \int_{-1}^{1} \frac{\dfrac{\mathrm{e}^{2\alpha\tau}(1 + x)}{[\mathrm{e}^{\alpha\tau}(1 + x) + 1 - x]^4}}{\left[\dfrac{-12\,\mathrm{e}^{\alpha\tau}(1 + x) - 4(1 - x)}{\{\mathrm{e}^{\alpha\tau}(1 + x) + 1 - x\}^3} + 2 + x\right]^{\frac{1}{2}}} \mathrm{d}x. \tag{9}$$

This expression for the Sherwood number is equivalent to equations (34) and (35), Ref. [8], and reduces to the same limiting expressions for very small and very large times.

When the controlling resistance is in the dispersed phase, the above expression reduces to that of equation (37), Ref. [8]. Other approximate solutions for the problem of negligible external phase resistance and creeping flow have been provided by Kronig and Brink [6] and by Johns and Beckman [5]. The latter solutions were obtained numerically for Péclet numbers from 0 to 640. Comparison of the various models with the numerical results obtained by Johns and Beckmann for a representative Péclet number are presented in Fig. 1.

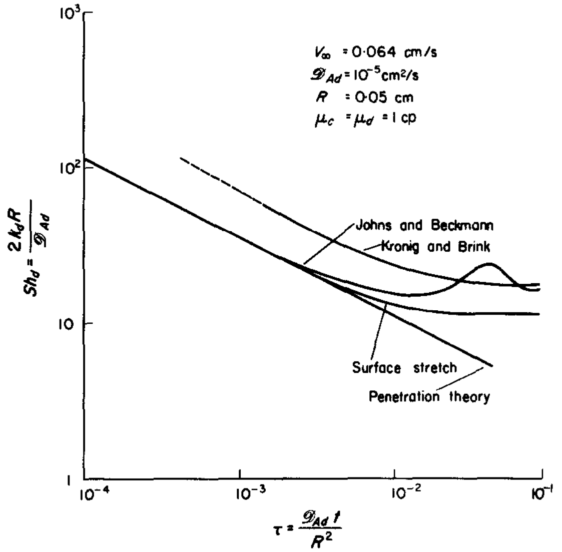

FIG. 1. Comparison of different methods for calculating time-dependent Sherwood numbers.

It can be seen that for small times, equation (7) agrees exactly with the penetration theory. However, at intermediate times (not uncommon in industrial sieve-tray extractors) the agreement with the numerical results is poor. In the large-time, large-Péclet-number limit, the results become exact only when agreeing with the Kronig and Brink theory (i.e. $Pe_d \approx 1500$).

Agreement of the surface stretch theory with the results of Johns and Beckmann can be achieved only under limited circumstances. The probable cause of such disagreement is that the recirculation of the solute within the droplet is not adequately accounted for. This has also been evident in other systems such as falling films [4] in which the mass-transfer is limited in one phase. It appears then, that the only systems to which the above theory may be applied are those in which the continuous phase mass-transfer resistance is predominant.

## APPLICATION OF THE SURFACE-STRETCH MODEL AT HIGH REYNOLDS NUMBERS

Although velocity profiles are not known in detail for high Reynolds number flows the boundary-layer solution of Chao [2] and Moore [7] is to be preferred over that obtained from potential flow theory. Such a solution provides the proper velocity and velocity-gradient behaviour in the interfacial region, whereas the potential flow solution does not. Application of the surface-stretch model using the "corrected" velocity profile at the interface gives, for negligible continuous phase resistance (see Appendix):

$$Sh_d = \sqrt{\left(\frac{3}{4\pi} Pe_d\right)} \int_{\cos\theta_s}^{1} \frac{f(x)}{\sqrt{\left(\int_x^{x_0} f(x^*)\,\mathrm{d}x^*\right)}}\,\mathrm{d}x \tag{10}$$

where

$$f(x) = 1 - x^2 - B(2 + x)^{\frac{1}{2}}(1 - x) \tag{11}$$

$$\int_x^{x_0} f(x^*)\,\mathrm{d}x^* = x^* - \frac{x^{*3}}{3} - B[\tfrac{2}{3}(2 + x^*)^{\frac{3}{2}} + \tfrac{2}{15}(4 - 3x^*)(2 + x^*)^{\frac{3}{2}}]\Big|_x^{x_0} \tag{12}$$

$$\cos\theta_s = \frac{B^2 - 2 + B\sqrt{(B^2 + 4)}}{2} \tag{13}$$

and

$$B = \frac{4}{3\sqrt{(\pi Re)}} \frac{\left[2 + 3\frac{\mu_d}{\mu_c}\right]}{1 + \left(\frac{\rho_d \mu_d}{\rho_c \mu_c}\right)^{\frac{1}{2}}} = \frac{4}{3\sqrt{(\pi Re)}} b. \tag{14a, b}$$

The integration over $x$ in equation (10) is to be performed at constant time; such a restraint being expressed in terms of $x$ and $x_0$ as:

$$\begin{aligned} -\tfrac{3}{4} Pe\,\tau = &-\frac{1}{2 - B\sqrt{3}} \ln\left\{\frac{(\sqrt{3}) - \sqrt{(2 + x)}}{(\sqrt{3}) - \sqrt{(2 + x_0)}}\right\} \\ &- \frac{1}{2 + B\sqrt{3}} \ln \frac{(\sqrt{3}) + \sqrt{(2 + x)}}{(\sqrt{3}) + \sqrt{(2 + x_0)}} \\ &+ \frac{2}{4 - 3B^2} \ln \frac{1 + x - B\sqrt{(2 + x)}}{1 + x_0 - B\sqrt{(2 + x_0)}} \\ &+ \frac{4B}{(4 - 3B^2)\sqrt{(4 + B^2)}} \left[\ln\left\{\frac{2\sqrt{(2 + x)} - B - \sqrt{(B^2 + 4}}{2\sqrt{(2 + x_0)} - B - \sqrt{(B^2 + 4)}}\right\}\right. \\ &\left. - \ln\left\{\frac{2\sqrt{(2 + x)} - B + \sqrt{(B^2 + 4)}}{2\sqrt{(2 + x_0)} - B + \sqrt{(B^2 + 4)}}\right\}\right]. \end{aligned} \tag{15}$$

In the integral of equation (10), $\theta_s$ is that angle at which the interfacial velocity becomes equal to zero. It has been suggested by Winnikow and Choa [10] that such a position be used as a rough estimate of the locus of boundary-layer separation. Thus, the expression for the Sherwood number in equation (10) does not contain the contribution from the zone of boundary-layer separation at the rear of the drop. This expression has been evaluated numerically, and the results for representative Reynolds numbers are shown in Fig. 2 along with Ruckenstein's results for potential flow theory.

Equation (10) simplifies to the proper limiting expressions for small and large time. For small time, the Sherwood number becomes equivalent to that given by the penetration theory [3], i.e.

$$Sh_d = \frac{1 - \cos\theta_s}{\sqrt{(\pi\tau)}}. \tag{16}$$

For large times, the limiting expression becomes

$$\begin{aligned} Sh_d = \sqrt{\left(\frac{3}{\pi} Pe_d\right)} \Big\{ &\tfrac{2}{3} - \cos\theta_s + \frac{\cos^3\theta_s}{3} \\ &- B[\tfrac{2}{3}\{(3)^{\frac{3}{2}} - (2 + \cos\theta_s)^{\frac{3}{2}}\} + \tfrac{2}{15}\{(3)^{\frac{3}{2}} \\ &- (4 - 3\cos\theta_s)(2 + \cos\theta_s)^{\frac{3}{2}}\}]\Big\}^{\frac{1}{2}}. \end{aligned} \tag{17}$$

## VELOCITY TRANSIENTS

The above correlations, like most of those available in the published literature [3, 5, 6, 8], are based on the assumption of steady-state flow. During a recent analysis of unsteady creeping flow [9] it has, however, come to our attention that transients in the interfacial velocity distribution could have a significant effect upon transient mass-transfer behaviour. The utility uf equations (7) and (10) is therefore still subject to doubt, even when the predominant mass-transfer resistance is in the continuous phase. The effect of velocity transients should be investigated further.

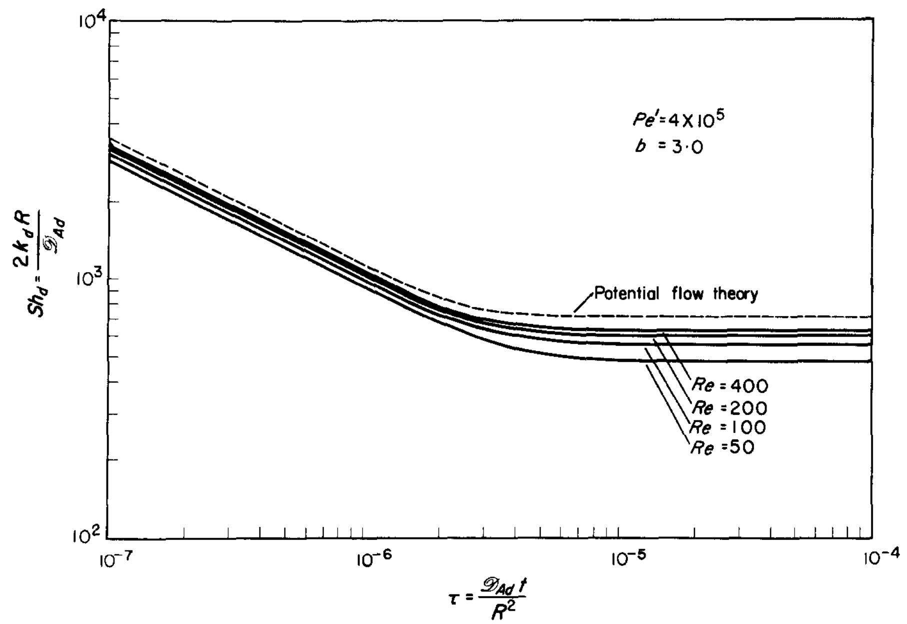

FIG. 2. Calculations based on the surface-stretch model for high Reynolds number flows.

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## APPENDIX

Equations (7) and (17) can be obtained from equation (4) utilizing a prior knowledge of the tangential interfacial velocity for fluid–fluid spherical systems. From equations (2) and (3) we have:

$$\left(\frac{\partial S}{\partial S_0}\right)_t = \left(\frac{\partial \cos\theta}{\partial \cos\theta_0}\right)_t \tag{A.1}$$

where it must be remembered that the position $\theta$ of any surface element can be expressed in terms of its original position $\theta_0$ and the time $t$. The change of position of a fluid element along the interface is given by:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = (v_\theta)_0/R. \tag{A.2}$$

Where the tangential interfacial velocity for creeping flow is:

$$(v_\theta)_0 = \frac{1}{2}\frac{\mu_c}{\mu_c + \mu_d} V_\infty \sin\theta. \tag{A.3}$$

The "corrected" interfacial velocity for high Reynolds number flows is [10]:

$$(v_\theta)_0 = \tfrac{3}{2} V_\infty \sin\theta \left[1 - B\frac{(\frac{2}{3} - \cos\theta + \frac{1}{3}\cos^3\theta)^{\frac{1}{2}}}{\sin^2\theta}\right]. \tag{A.4}$$

Integrating equation (A.2) between the limits of $\tau = 0$ and $\tau = \tau$ gives the expressions for $(\partial S/\partial S_0)_\tau$:

(Creeping flow) $\left(\frac{\partial S}{\partial S_0}\right)_\tau$

$$= \frac{4\,\mathrm{e}^{\alpha\tau}}{[\mathrm{e}^{\alpha\tau}(1 + \cos\theta_0) + 1 - \cos\theta_0]^2}. \tag{A.5}$$

(High *Re* flow) $\left(\frac{\partial S}{\partial S_0}\right)_\tau$

$$= \frac{1 - \cos^2\theta - B(2 + \cos\theta)^{\frac{1}{2}}(1 - \cos\theta)}{1 - \cos^2\theta_0 - B(2 + \cos\theta_0)^{\frac{1}{2}}(1 - \cos\theta_0)}. \tag{A.6}$$

where $(\partial S/\partial S_0)_\tau$ for high Reynolds numbers is an implicit function of $\theta_0$ and $\tau$ through equation (15) by replacing $x$ by $\cos\theta$ and $x_0$ by $\cos\theta_0$.

Equation (7) follows readily from the substitution of equation (A.5) into equation (4) and subsequent manipulation. It is not feasible to obtain the analogous expression for the high Reynolds number case because equation (A.6) is only an implicit function of time. However, it is possible to obtain equation (10) from equation (4) by noting that:

$$(\mathrm{d}t)_{\cos\theta_0} = \left(\frac{\partial t}{\partial \cos\theta}\right)_{\cos\theta_0} (\mathrm{d}\cos\theta)_{\cos\theta_0} \qquad \text{(A.7)}$$

$$(\mathrm{d}\cos\theta_0)_t = -\left(\frac{\partial\cos\theta_0}{\partial t}\right)_{\cos\theta} \times \left(\frac{\partial_t}{\partial\cos\theta}\right)_{\cos\theta_0} (\mathrm{d}\cos\theta)_t. \qquad \text{(A.8)}$$

Equation (17) is the large time limiting case of equation (10) and is obtained merely be replacing the $x_0$ of equation (10) by one. Physically, this means that for large time, only those surface elements formed very near the stagnation point ($\theta = 0$) will measurably contribute to the mass-transfer process.