Mass Transfer to a Surfactant-Covered Bubble or Drop

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Mass transfer of a solute to a rising spherical bubble (or drop) with surfactant on its interface is of fundamental importance in many separation processes in environmental engineering, chemical and biochemical processing, and minerals refining. It has been the subject of considerable research since the early work of Frumkin and Levich (1947). Schecter and Farley (1963) used an integral formulation of the convection−diffusion equation in combination with an assumed polynomial form for the diffusing species concentration profile. They calculated the dimensionless mass-transfer rates for different values of an interfacial-tension gradient group in the range of bulk Péclet numbers between 5×10^{-2} and 5×10^{3}. Lochiel (1965) developed an analytic expression for the Sherwood number in terms of the bulk Péclet number and very small values of the interfacial tension gradient group. More recently, Clift et al. (1978) and Quintana (1992) determined the mass-transfer rate to a bubble when a stagnant cap develops (typically due to slow surfactant diffusion along the surface of the bubble), a common occurrence for large bubbles. Clift et al. (1978) also give expressions that fit numerical calculations for the two extreme cases of mass transfer to a rigid sphere and to a spherical bubble with a freely mobile interface. Brunn and Isemin (1984) presented asymptotic and numerical results for the dimensionless mass-transfer rate in terms of the bulk Péclet number and the surfactant retardation parameter of Levich (1962); their final expression becomes inaccurate for large but finite values of the retardation parameter.

In the current work, we examine the mass transfer of a diffusing species toward a small spherical bubble (or drop) translating in Stokes flow with a surface-active agent adsorbed on its interface. Mass transfer of surfactant between the interface and bulk fluid is assumed to be negligible, implying that the surfactant is nearly insoluble in the bulk or that adsorption/desorption is slow. Small deviations in surface coverage are assumed, but the retardation parameter and bulk Péclet number are arbitrary. This situation is of particular relevance in the case of very small gaseous bubbles (with diameters less than approximately 50 μm) rising in an aqueous medium; practical examples include electroflotation and microflotation.

Problem Statement and Solution

The steady-state convection-diffusion equation describing the transport of insoluble surfactant on the surface of the translating bubble is (Levich, 1962)

$$\nabla_s\cdot[\Gamma \boldsymbol{v}_0 - D_s\nabla\Gamma] = 0, \tag{1}$$

where $\boldsymbol{v}_0$ is the fluid tangential velocity relative to the center of the moving bubble; D_s is the isotropic surfactant surface diffusivity; and Γ is the surfactant surface concentration. The interfacial tension is a function of the local surface coverage: $\sigma=\sigma(\Gamma)$. The deviation in surface coverage is small compared to the average value when surface diffusion is strong, $Pe_s = Ua/D_s \ll 1$, or when the Marangoni stresses are strong, $Ma = B\Gamma_0/\mu U \gg 1$ (Cristini et al., 1998; Blawzdziewicz et al., 1999), where Pe_s is the surface Péclet number, Ma is the Marangoni number, U is the bubble translational velocity, a is its radius, μ is the external fluid viscosity, Γ_0 is the average surfactant surface concentration, and $B = -\partial\sigma/\partial\Gamma$ is assumed constant for small variations in surface concentration. Note that $B = RT$ for nonionic surfactants at low surface coverages and without long-range interactions (Levich, 1962), where R is the universal gas-law constant and T is the absolute temperature.

The tangential stress jump at the bubble interface yields the relation $\boldsymbol{\tau}_0 = \nabla_s\sigma = -B\nabla_s\Gamma$, where $\boldsymbol{\tau}_0$ is the tangential stress acting on the bubble interface. Substituting this relation in Eq. 1 with $\Gamma \cong \Gamma_0$ yields

$$\boldsymbol{v}_0^* = \boldsymbol{\tau}_0^*/A \tag{2}$$

on the surface of the bubble, where $\boldsymbol{v}_0^* = \boldsymbol{v}_0/U$, $\boldsymbol{\tau}_0^* = a\boldsymbol{\tau}_0/\mu U$, and $A = B\Gamma_0 a/\mu D_s = MaPe_s$ is the surface retardation parameter. For small values of A, the surfactant has little effect on the free-slip flow along the bubble interface, whereas Marangoni stresses due to the surfactant gradient retard interfacial motion at large A. Equation 2 represents a

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Maxwell-slip boundary condition, for which Lamb (1945) gives the Stokes-flow solution for the velocities (made dimensionless by $U = 2(A+3)\Delta\rho a^2 g/[9(A+2)\mu]$, where g is the gravitational acceleration and $\Delta\rho$ is the density difference between the external and internal fluids) of the surrounding fluid relative to the bubble center in the radial and tangential directions, respectively:

$$u^* = -\left[1 + \frac{A}{2(y^*+1)^3(A+3)} - \frac{3}{2(y^*+1)}\frac{(A+2)}{(A+3)}\right]\cos\theta, \tag{3}$$

$$v^* = \left[1 - \frac{A}{4(y^*+1)^3(A+3)} - \frac{3}{4(y^*+1)}\frac{(A+2)}{(A+3)}\right]\sin\theta, \tag{4}$$

where $y^* = (r-a)/a$ is the dimensionless distance from the bubble surface, r is the length of the position vector from the bubble center, and θ is the angle that the position vector makes with the direction of bubble translation. We note that Eqs. 3–4, and all of the subsequent mass-transfer results, apply for spherical drops as well as bubbles, provided that the retardation parameter is defined as $A = 3\lambda + MaPe_s$, where λ is the ratio of internal and external fluid viscosities (Levich, 1962; Brunn and Isemin, 1984).

The conservation equation for the solute or diffusing species in the surrounding fluid is, at steady state,

$$u^*\frac{\partial c^*}{\partial y^*} + \frac{v^*}{(y^*+1)}\frac{\partial c^*}{\partial\theta} = \frac{1}{(y^*+1)^2}\frac{1}{Pe} \times\left[\frac{\partial}{\partial y^*}\left((y^*+1)^2\frac{\partial c^*}{\partial y^*}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial c^*}{\partial\theta}\right)\right], \tag{5}$$

subject to the boundary conditions

$$c^*(\theta,0) = 1, \qquad c^*(\theta,\infty) = 0, \qquad \text{and} \qquad \frac{\partial c^*}{\partial\theta} = 0 \quad \text{at} \quad \theta = 0, \pi. \tag{6}$$

Here, the dimensionless solute concentration is defined as $c^* = (c - c_\infty)/(c_s - c_\infty)$, where c_∞ is the bulk concentration and c_s is the equilibrium concentration in the fluid adjacent to the surface of the bubble. The bulk Péclet number is $Pe = Ua/D$, with D being the diffusion coefficient of the solute in the bulk liquid. Equations 5–6 were solved through an implicit finite difference numerical scheme for the concentration profile, with the radial and tangential fluid velocities given by Eqs. 3–4; the parameters A and Pe were varied over wide ranges.

Results and Discussion

Figure 1 shows lines of constant dimensionless concentration surrounding a translating bubble in Stokes flow at $Pe = 10$ for different values of the surface retardation parameter. A mass-transfer boundary layer (which becomes thinner for larger Pe) forms on the front hemisphere, and a concentration wake is present behind the bubble. For small values of the surface retardation parameter, the slip flow along the interface allows for a higher fluid velocity toward the front of the bubble, so that the concentration profile is steeper and the mass-transfer rate is higher than for large values of A. In the rear of the bubble, however, the increased slip flow along the interface at smaller values of A allows for greater radial velocities away from the bubble, so that the isoconcentration curves for different values of A cross each other.

Figure 2 shows the variation of the local Sherwood number, $Sh_\theta = -2(\partial c^*/\partial y^*)_{y^*=0}$, with angular position for the case of boundary-layer mass transfer at $Pe = 10^5$. Marked differences exist in the local rates of mass transfer for different degrees of surface retardation. In the region of incident flow $(-\pi/2 < \theta < \pi/2)$, where there is a thin concentration boundary layer adjacent to the surface of the bubble, the local mass-transfer rate is enhanced dramatically by the interfacial flow, which increases the radial convection of solute and sharpens the concentration gradient.

In Figure 3, the area-averaged Sherwood number, $Sh = (1/2)\int_0^\pi Sh_\theta \sin\theta\, d\theta = 2\,ka/D$, where k is the area-averaged mass-transfer coefficient, is presented as a function of the bulk Péclet number for various degrees of surface retardation. Also included are the asymptotic results of Acrivos and Goddard (1965) for a solid spherical particle and of Hirose

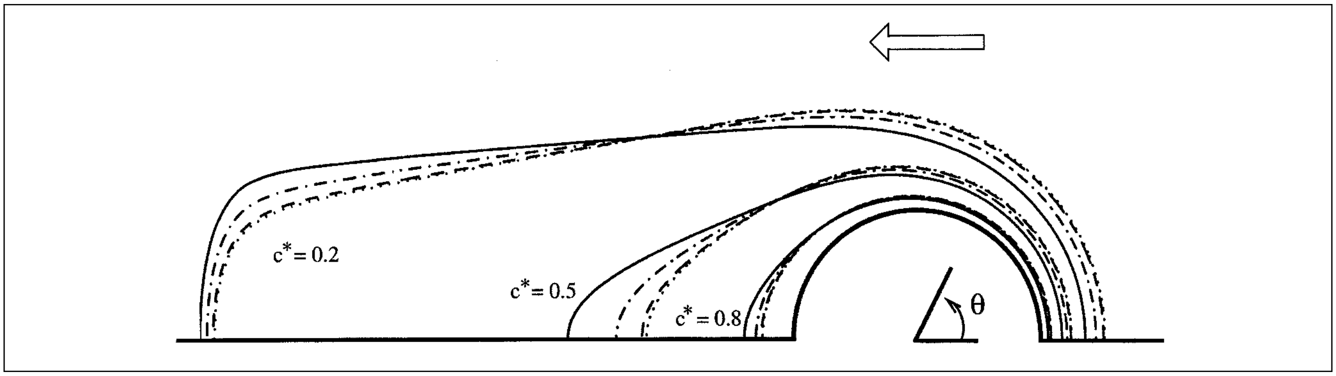

Figure 1. Lines of constant dimensionless concentration for $Pe = 10$, with $A = 0$ (solid lines), 5 (dot dashed lines), 50 (dashed lines), and ∞ (dotted lines).

The arrow shows the primary direction of fluid flow relative to the bubble.

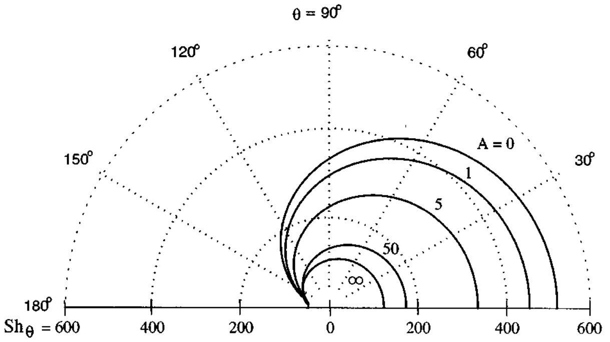

Figure 2. Dependence of the local Sherwood number on the angle from the front stagnation point at $Pe = 10^5$ and different surface retardations.

(1978) for a surfactant-free bubble. These asymptotic relations are only applicable for $Pe \gg 1$ and constitute the limiting values for the cases of no interfacial motion ($A = \infty$) and unretarded interfacial motion ($A = 0$), respectively. Also contained in Figure 3 is the expression of Lochiel (1965), suitable for small deviations from free interfaces. Since Lochiel's derivation assumes that the tangential velocity at the surface of the bubble is substantially larger than the change in velocity across the concentration boundary layer, it fails for small and modest Péclet numbers, as the boundary layer is then no longer thin; the expression also fails for large values of A, because the interfacial velocity is then small. The expression developed by Brunn and Isemin (1984), as given by their Eqs. 44a–44b, is also included and shows good agreement with the present numerical solution for $A \leq O(10)$. For larger values of the surface retardation parameter, however, this expression greatly overpredicts the dimensionless mass-transfer rate and gives values that increase rather than decrease with increasing surface retardation. The difficulty in obtaining accurate results for $A \gg 1$ arises because the rigid-sphere limit of $A = \infty$ [$F_0 = 1$, in the notation of Brunn and Isemin (1984)] is singular in the sense that the small but nonzero interfacial velocity for large but finite A can have a significant effect on the mass-transfer rate when the concentration boundary layer is sufficiently thin.

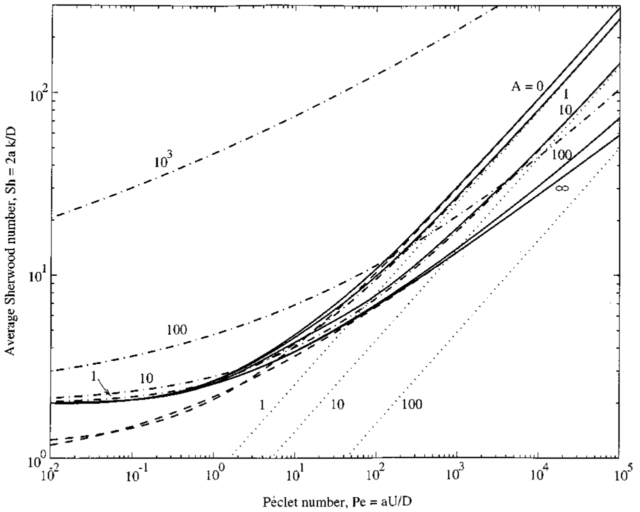

Figure 3. Average Sherwood number as a function of the Péclet number for different values of the surface retardation parameter.

The solid lines are the present numerical solution for $A = 0$, 1, 10, 100, and ∞ (top to bottom); the dashed lines are the asymptotic solutions of Hirose (1978) and Acrivos and Goddard (1965) for $A = 0$ and ∞, respectively; the dotted lines are from the expression of Lochiel (1965) for $A = 1$, 10, and 100 (top to bottom); and the dot–dashed lines are from the expression of Brunn and Isemin (1984) for $A = 1$, 10, 100, and 1,000 (bottom to top at small Pe).

For the limit of $Pe \ll 1$, the diffusion-dominated result $Sh \cong 2$ is independent of the retardation parameter A, since the flow field has negligible effect on the mass-transfer process in this limit. As seen in Figure 3, the effect of surface retardation on the mass-transfer rate becomes more marked as the bulk Péclet number increases. Higher Péclet numbers imply thinner concentration boundary layers restricted to regions very close to the surface of the bubble, where the influence of interfacial motion on the fluid velocity profiles is more pronounced. For large solutes or colloids with small diffusivities, it may be quite important to quantitatively consider the effects of an adsorbed surfactant on the bubble surface mobility and resulting mass-transfer rate.

The physical and dimensionless parameters of interest are shown in Table 1 as a function of bubble diameter for two extreme cases of high surface coverage ($\Gamma_0 = 10^{-10}$ mol/cm^2) of a large surfactant with low diffusivity ($D_s = 10^{-6}$ cm^2/s)

Table 1. Physical and Dimensionless Parameters for Bubbles Rising in Water at 20°C

$2a$ (μm)	U (cm/s)	Re	A	Ma	Pe_s	Pe
2	2.2×10^{-4}	2.2×10^{-6}	2.8×10^{4}	1.3×10^{6}	0.022	1.0
	2.6×10^{-4}	2.6×10^{-6}	2.8	1.1×10^{3}	2.6×10^{-3}	1.0
5	1.4×10^{-3}	3.4×10^{-5}	7.0×10^{4}	2.1×10^{5}	0.34	25
	1.6×10^{-3}	3.8×10^{-5}	7.0	180	0.038	25
10	5.5×10^{-3}	2.8×10^{-4}	1.4×10^{5}	5.0×10^{4}	2.8	100
	5.8×10^{-3}	3.0×10^{-4}	14	47	0.30	100
20	0.022	2.2×10^{-3}	2.8×10^{5}	1.3×10^{4}	22	1.0×10^{3}
	0.023	2.3×10^{-3}	28	12	2.3	1.0×10^{3}
50	0.14	0.034	7.0×10^{5}	2.1×10^{3}	340	2.5×10^{4}
	0.14	0.034	70	2.1	34	2.5×10^{4}

Note: For each pair of entries, the top entry is for $\Gamma_0 = 10^{-10}$ mol/cm^2 and $D_s = 10^{-6}$ cm^2/s, while the bottom entry is for $\Gamma_0 = 10^{-13}$ mol/cm^2 and $D_s = 10^{-5}$ cm^2/s. The bulk Péclet number, $Pe = aU/D$, is based on $D = 2.1\times10^{-8}$ cm^2/s for Brownian diffusion of a particle with 0.1 μm radius.

and low surface coverage ($\Gamma_0 = 10^{-13}$ mol/cm^2) of a smaller surfactant with higher diffusivity ($D_s = 10^{-5}$ cm^2/s). For the first case, $A \gg 1$ for all non-Brownian bubbles, and the high surface retardation causes the results to be close to those for a rigid sphere. For the second case, however, $A \leq 100$ is achieved, and the effects of surface mobility on the mass-transfer rate can be significant. In all cases, $Re = \rho U a/\mu \ll 1$ for $2a \leq 50$ μm, and the constraint $Pe_s \ll 1$ or $Ma \gg 1$ is also met in all cases except for the largest bubbles in this range when the surfactant coverage is very small. For drops with clean interfaces, $A = 3\lambda$, and so arbitrary interfacial mobilities may be achieved by varying the viscosity ratio. Finally, we note that, although $Pe_s \ll 1$ or $Ma \gg 1$ was assumed in the analysis, the limit $Ma \ll 1$ for very dilute surfactant coverages (with Pe_s arbitrary) is also described by the present results with $A = 3\lambda$, since in this case the Marangoni stresses are small (except for in a very small region near the rear-stagnation zone where the surfactant will accumulate if $Pe_s \gg 1$).

The numerical results obtained in this work for the range of values for Pe and A shown in Figure 3 were correlated through a simple analytical expression:

$$Sh = 2.0 + \alpha Pe^{\beta}, \tag{7}$$

where

$$\alpha(A) = \frac{5.49}{A+6.10} + \frac{A}{A+28.64} \quad \text{and} \quad \beta(A) = \frac{0.35A+17.21}{A+34.14}. \tag{8}$$

These equations are accurate within approximately 10% for all values of the bulk Péclet number and surface retardation parameter.

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