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The effect of surface blocking on mass transfer from a stagnant cap drop

G. C. QUINTANA
AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974, U.S.A.

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Abstract—Numerical results for single-drop exterior mass transport of a solute from a surfactant covered drop to the continuous phase are presented. In particular the effect of physicochemical surface blocking is determined by considering the case in which the adsorbed surfactant accumulates at the rear of the translating drop. The stagnant cap velocity profiles are used to describe convective transport. Surface blocking is incorporated through the choice of a zero flux boundary condition on those portions of the drop where surfactant is present. Finite element numerical results for the Sherwood numbers as a function of Peclet number ($Pe \leqslant 10^4$) and stagnant cap angle, ϕ, show that for surface coverages greater than 0.1π, the effect of surface blocking cannot be ignored. For a Peclet number equal to 10^4 and $\phi = 0.5\pi$, the mass transfer coefficients calculated under the assumption that the presence of surfactant reduced convection in the vicinity of the drop without inhibiting the interfacial transport of solute, are found to overestimate the rate of solute mass transfer by as much as 20%.

1. INTRODUCTION

THE EFFECT of trace amounts of surface-active agents on mass transfer from single drops has been the subject of a large number of investigations. Interest in this problem has been prompted by our lack of understanding of the transport mechanisms which are responsible for the hindered mass transfer efficiency observed in commercial extraction processes which take place in the presence of trace contaminants. Recently, concern for fully comprehending the details of this transport phenomenon has been renewed due to the importance of assessing the effect of organic contaminants, i.e. such as those found in acid rain, on the mass transport and aqueous phase reaction of gases in liquid-water cloud drops [1, 2].

Experimental studies on single-drop systems date back to the work of Garner and Hale [3] and Lindland and Terjesen [4]. Garner and Hale studied the effect of the presence of the surface-active agent *Teepol* on the rate of extraction of diethylamine from toluene drops to the aqueous continuous phase. The *exterior* phase mass transport of diethylamine was found to be significantly reduced by the presence of small amounts of surfactant. The maximum resistance to diethylamine transport corresponded to a *Teepol* concentration of 1.5×10^{-2} ml per 100 ml of water, for which a 55% reduction in solute extraction relative to that in the clean system was reported. In the work of Lindland and Terjesen, the addition of much smaller amounts of sodium oleyl-*p*-anisidenesulphonate were found to decrease the rate of iodine extraction from the aqueous phase to carbon tetrachloride drops to a much larger extent than that indicated by the results of Garner *et al.* In these *interior* solute mass transport experiments, the addition of as little as 6×10^{-5} g of surfactant per 100 ml of water reduced the mass transfer coefficient to as little as 33% of the clean system value. Although strict comparison of these two studies is precluded by the fact that the hydrodynamics which govern the exterior solute mass transfer problem differs from that which determines the role of convection for interior dropwise mass transport, the discrepancy between the reported order of magnitude of surfactant which produced these effects is surprisingly large. This can perhaps be explained by the fact that the adsorption behavior of the two surfactants differs. However, the lack of data which precisely correlates the drop surface coverage, i.e. the actual amount of adsorbed surfactant, with the experimentally determined mass transfer coefficients, makes it impossible to determine if it is the surfactant physical chemistry or possible experimental error which is responsible for these reported differences. Despite this reservation, the order of magnitude of the mass transfer reductions reported by these authors has been substantiated by a number of subsequent papers, the most recent being the exterior drop mass transfer study of Mekasut *et al.* [5].

The mass transfer reductions observed for these single-drop systems have been attributed to two different mechanisms: (1) the decrease of convection at the drop interface which results from surfactant adsorption and (2) the interfacial barrier to transport due to the physical presence of adsorbed surfactant. The ability of an adsorbed surfactant monolayer to physically impede the rate of water evaporation of quiescent ponds and reservoirs, has long been exploited. In a number of classic experiments [6–8] researchers have attempted to quantify the extent of mass transfer reduction arising from the interfacial steric hindrance due to surface-active agents, as a

NOMENCLATURE

$c(r,\theta)$	solute concentration
$C(r,\theta)$	dimensionless solute concentration
c_i	solute concentration in outside sublayer near drop
C_k^*	kth order stagnant cap stream function coefficient
c_0	disperse phase solute concentration
c_∞	solute concentration far away from drop
D	continuous phase solute diffusion coefficient
K	distribution coefficient
$P_k(\cos\theta)$	kth order Legendre polynomial
Pe	continuous phase Peclet number, $2U_sR/D$
r	radial coordinate
R	drop radius
Sh	Sherwood number
$u_r(r,\theta)$	dimensionless continuous phase radial velocity
u_s	interfacial tangential velocity
$U_s(\phi)$	stagnant cap drop terminal velocity
U_{STOKES}	solid sphere terminal velocity
$u_\theta(r,\theta)$	dimensionless continuous phase tangential velocity.

Greek symbols

$\Gamma(\theta)$	interfacial surfactant concentration
θ	tangential coordinate
κ	ratio of drop to continuous phase viscosity
$\mu, \hat{\mu}$	continuous and disperse phase viscosity
ϕ	stagnant cap angle
$\psi, \hat{\psi}$	continuous and disperse phase stream functions.

function of surfactant film thickness and alkyl chain length. A number of more recent studies assert that only bulk insoluble surfactants are capable of physically inhibiting the interfacial transfer of some solutes [9, 10], while bulk soluble surfactants produce no discernible barrier for the transport of small diffusing species [10, 11]. To date, this contention has neither been confirmed nor disproved. Few studies have considered the question of how the interfacial steric hindrance due to the adsorption of bulky surfactant molecules will affect mass transport between two phases which are in relative motion. Huang and Kintner [12] addressed this point experimentally by observing the degree of surfactant coverage and the extent of internal circulation of water drops and correlating these data with the rate of cyclohexane extraction to the drops. They found that the mass transfer reductions strongly depended on both the hydrodynamics and the percentage of interfacial drop area covered by the contaminant.

In this paper we examine the effect of an adsorbed surfactant monolayer on mass transfer from a sedimenting fluid drop to the surrounding continuous phase. In particular we determine the extent to which the effect of surface blocking will influence solute mass transport. In this context the term surface blocking encompasses a variety of physicochemical mechanisms by which a surfactant monolayer can hinder interfacial transport. For a particular system, this will be a complex function of surfactant molecule size, since this will influence the degree of steric hindrance which can be affected by the molecule. The effect of surface blocking is incorporated through an appropriate choice of the boundary conditions. If we consider the case in which the adsorbed surfactant monolayer is fully impenetrable to solute transport, then we can assume a zero solute flux boundary condition on portions of the drop where surfactant is present.

We treat the case of mass transfer from a surfactant covered fluid drop in which the solubility of the contaminant in both the continuous and drop phases is kinetically limited, i.e. desorption of surfactant from the interface is slow. In this limit, the equilibrium distribution of surfactant has been shown by a number of investigators to be highly nonuniform [12–18]. The surfactant is driven to the drop rear by interfacial convection where it forms a stagnant cap. The analytical expressions for the stream functions which describe the flow in and around the stagnant cap drop were derived by Sadhal and Johnson [19] in the limit of low Reynolds number. Finite element numerical integration is used to solve for the mass transfer Sherwood numbers for the problem of drop to continuous phase solute extraction in the presence of adsorbed surfactant. We compare these results to those obtained for the same problem under the assumption that physicochemical surface blocking is negligible.

2. PROBLEM FORMULATION

2.1. *Fluid mechanics*

We consider mass transport of a solute from a surfactant covered fluid drop to the continuous phase. The velocity and concentration fields are referenced to a spherical coordinate system the origin of which is fixed at the drop center. We assume that the surface tension forces are large relative to viscous forces normal to the interface which would act to deform the drop. Thus the drop interface ($r = R$) can be assumed to remain spherical.

Surfactants present even at low concentrations reduce the interfacial and terminal velocities of a settling drop to values which are well below those predicted by the Hadamard–Rybczynski analysis. This reduced convection results from the interfacial tension gradient forces which arise from the uneven dis-

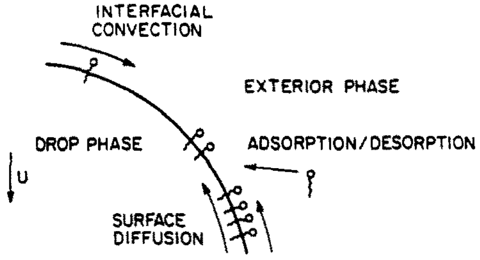

FIG. 1. Effect of surface convection, surfactant adsorption/desorption, and surface diffusion on the distribution of surfactant.

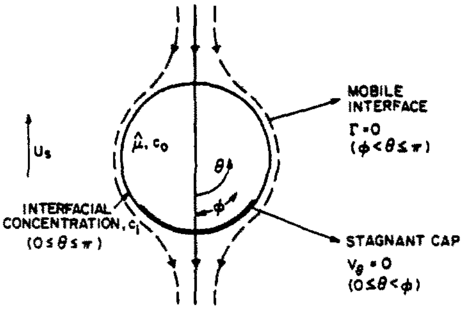

FIG. 2. Mass transfer of a solute from a rising stagnant cap bubble.

tribution of surfactant at the drop interface. In general, the local surfactant concentration is determined by three competing mechanisms: surface diffusion, adsorption kinetics and interfacial convection (see Fig. 1).

In the limit of low Reynolds number, Levich [20] obtained an analytical solution for flow in and around a surfactant covered drop for the limiting case in which the surface concentrations vary only slightly from their equilibrium (i.e. non-translating) value. The 'uniform retardation' analysis adopted by Levich is suitable only when the transfer of surfactant between the bulk and the interface is not kinetically or diffusion limited. When the kinetics of surfactant desorption is slow relative to adsorption, or when the diffusive transport of surfactant from the bulk to the interface is rapid, i.e. large bulk Peclet number for the surfactant, the surfactant accumulates at the interface and consequently a uniform distribution at the surface cannot be maintained. Experimental observation by Savic [13], Garner and Skelland [14], Griffith [16] and others has shown that in this limit the surfactant will not be distributed evenly over the drop surface but instead will collect towards the rear forming a 'stagnant cap', while the rest of the drop surface remains mobile.

The determination of the equilibrium distribution of surfactant and its effect on the drop translational motion for the limiting case of adsorbed contaminant which is confined to the interface, was first addressed by Savic [13]. In this limit, both surface diffusion and the rate of surfactant adsorption–desorption from the bulk are negligible relative to surface convection. The distribution of surfactant, $\Gamma(\theta)$, is determined by integration of the steady surface mass transport equation

$$\nabla_s \cdot (u_s \Gamma) = 0 \tag{1}$$

where u_s is the surface velocity and Γ the surfactant concentration. The solution of equation (1) which is consistent with stagnant cap formation is given by

$$u_s = 0 \quad 0 \leqslant \theta < \phi \tag{2}$$

and

$$\Gamma = 0 \quad \phi \leqslant \theta \leqslant \pi \tag{3}$$

where ϕ is the cap angle as shown in Fig. 2.

The solution of the problem of low Reynolds flow past a stagnant cap drop requires integration of the drop and continuous phase stream functions subject to the mixed boundary conditions (2) and (3). These equations are solved by expanding the inner and outer stream functions into two infinite spherical harmonic power series and then solving for the radial coefficients by matching the boundary conditions. Using this approach, Savic [13] and subsequently Davis and Acrivos [21] and Harper [22, 23], solved for the coefficients of the truncated stream function series to determine the velocity fields for this problem. Due to the discontinuity of the tangential velocity and divergence of the tangential stress in the vicinity of the cap edge, a large number of terms must be kept in the series in order to ensure convergence. Formulation of the creeping flow equations and boundary conditions as a set of dual series equations, by Sadhal and Johnson [19] permitted an exact analytical solution for the stream function coefficients as functions of the cap angle ϕ. These functions are given in the Appendix.

2.2. *Mass transport*

The effect of surfactants on spherical drop mass transfer was first addressed by Lochiel [24]. In this study, Sherwood number expressions for dropwise mass transport in the presence of surfactants were determined using boundary layer analysis. Lochiel formulated the boundary layer problem using the Levich [20] uniform retardation velocities. The validity of the boundary layer solution is thus limited to those situations in which the local concentration of surfactant varies little from the equilibrium concentration Γ_0. Although Lochiel's boundary layer results do predict that contaminants will produce reductions in mass transfer, the assumption of uniform surfactant distribution is at odds with the experimental observations of a number of researchers. In particular, in the mass transfer experiments of Huang and Kintner [12], the presence of a region of reduced interfacial mobility was clearly observed. In this instance and for many other multiphase systems of industrial importance, the uniform retardation velocity profiles provide an inadequate description of convective transport. For these systems the surfactant hindered hydrodynamics are more appropriately described by the stagnant cap velocities.

In this paper we determine the Sherwood number for solute mass transfer from a sedimenting stagnant cap drop to the continuous phase. We consider the limiting case of exterior phase mass transport. In this limit, the resistance to solute transport in the exterior or continuous phase is much greater than that presented by the dispersed phase. We assume that the initial solute concentration in the drop, c_0, is large relative to the amount which is extracted to the continuous phase. Thus the solute concentration within the disperse phase will remain essentially constant. In the exterior phase far away from the drop, the solute concentration is c_∞. We define the dimensionless exterior concentration to be $C(r, \theta)$, where $C(r, \theta)$ is given by

$$C(r,\theta) = \frac{c(r,\theta) - c_\infty}{c_i - c_\infty}. \tag{4}$$

Note that K is the distribution coefficient which defines the exterior solute concentration in the sublayer adjacent to the drop, i.e. $c_i = Kc_0$.

The distribution of solute in the continuous phase is found by integrating the dimensionless steady exterior convective diffusion equation

$$\left\{\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial C}{\partial\theta}\right\} = \frac{Pe}{2}\left\{u_r(r,\theta)\frac{\partial C}{\partial r} + \frac{u_\theta(r,\theta)}{r}\frac{\partial C}{\partial\theta}\right\} \tag{5}$$

where Pe is the continuous phase Peclet number and $u_r(r, \theta)$ and $u_\theta(r, \theta)$ the dimensionless exterior phase normal and tangential velocities as obtained from the stagnant cap outer stream function as given in the Appendix. Truncation of the outer stream function after 2000 terms proved adequate for the evaluation of the normal and tangential velocities. The continuous phase velocities $u_r(r, \theta)$ and $u_\theta(r, \theta)$ obtained from this truncated stream function were used in the governing equation. Note that in equation (5) the velocities are normalized with respect to the stagnant cap terminal velocity $U_s(\phi)$ which is given in the Appendix and the radial coordinate is nondimensionalized by R, the drop radius. Thus we define the Peclet number to be $Pe = 2U_sR/D$, where D is the solute continuous phase diffusion coefficient.

The governing convective diffusion equation is integrated subject to two sets of boundary conditions: one corresponding to negligible surface blocking and the other representing the situation of complete surface blocking or full solute impenetrability of the cap region. When surface blocking is negligible, the flux of solute through the interface is uninhibited. Integration of equation (5) subject to the boundary conditions

$$C(1,\theta) = 1.0 \tag{6}$$

at the interface, and

$$C(\infty,\theta) = 0.0 \tag{7}$$

far from the drop, suffice to describe the effect of reduced convection. The boundary conditions which describe surface blocking must include the zero flux condition at interfacial regions where surfactant is present. Thus the surface blocking boundary conditions are

$$C(1,\theta) = 1.0 \quad \phi < \theta \leqslant \pi \tag{8}$$

and

$$\frac{\partial C(1,\theta)}{\partial r} = 0.0 \quad 0 \leqslant \theta < \phi \tag{9}$$

at the interface, and equation (7) once again holds far from the drop. We numerically determine the mass transfer Sherwood number for reduced convection and for surface blocking as a function of the parameter ϕ. Note that the Sherwood number is given in terms of the dimensionless concentration gradient at the interface ($r = 1$) as

$$Sh = \int_0^\pi \left\{-\frac{\partial C}{\partial r}\right\}\bigg|_{r=1} \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta. \tag{10}$$

3. METHOD OF NUMERICAL SOLUTION

The exterior convective diffusion equation was integrated using a finite element software routine, TTGR (Transient Tensor Galerkin method for partial differential equations on Rectangles), which is built upon the PORT library of portable FORTRAN subprograms for numerical mathematics [25]. A powerful feature of TTGR is its use of a non-uniform mesh. This is particularly important for this problem, since a diffusion boundary layer of the order of Pe^{-n} will exist near the interface while the solute concentration will be nearly constant far away from the drop. Note that Lochiel and Calderbank [26] have determined n to be 1/2 for a drop with a mobile surface and 1/3 for a solid sphere. Use of a non-uniform mesh allows for a finer grid spacing where the solution varies rapidly and for a coarser grid where variations are slow. The importance of correctly choosing the position of node points within the boundary layer becomes more critical as the Peclet number increases

For our problem, the spherical domain was conformally mapped to the x–y plane. We initially chose a uniform mesh in x (i.e. normal to the drop) and a cosine mesh in y, tangent to the interface. This mesh was *automatically* refined in the direction normal to the interface using the routine SSAF (Smooth Spline Approximations to Functions). The grid optimization algorithm used by SSAF for obtaining nearly optimal spline approximations to functions for a fixed spline order and number of grid points, has been described by Schryer [27]. The optimization procedure used by SSAF involves calculation of the function (x) using a spline fit of order k and degree $k+1$, based on an initial choice of some mesh t. The error in this fit is

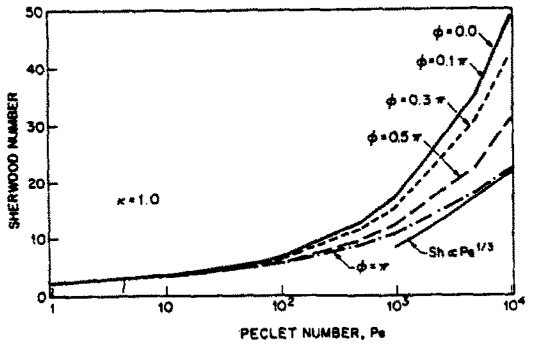

FIG. 3. Plot of the Sherwood number vs log Peclet number for $\phi = 0$, 0.1π, 0.3π, 0.5π, and π for reduced convection with the boundary layer result for the solid sphere [27] shown for a Peclet number greater than 10^3.

estimated, and new mesh points are chosen as those values which minimize the maximum error in $f(x)$. The equations are then resolved with the improved grid, and iterations in grid refinement continue until the largest error has fallen below some user specified tolerance e_u. In our simulations, optimization of the x grid was achieved by using SSAF to choose the mesh which fits $f(x)$ to an accuracy of 1% while holding the y mesh fixed. Estimation of the error in pertinent quantities such as the concentration and its gradients were then obtained by calculating the relative-changes in these quantities after each iteration. These quantities were found to converge and observation of the concentration gradient at the interface revealed a maximum error of 1.6% for the highest Peclet number that we studied, although errors of 1% or less were more typical. With the radial grid choice optimized by SSAF, integration of the convective mass transfer equations was possible for Peclet numbers up to 10^4. Oscillations in the solution which are usually associated with the hyperbolic nature of the equations for Pe as low as 2 [28] were not observed.

4. RESULTS AND DISCUSSION

Integration of the convective diffusion governing equation was carried out for several values of the cap angle, ϕ, and for Peclet numbers up to 10^4. The concentration profiles and Sherwood numbers were obtained for exterior transport both with and without surface blocking (i.e. with the constant solute concentration boundary condition (equations (6) and (7)) as well as for the mixed boundary conditions (equations (7)–(9))). For Peclet number equal to zero, the Sherwood number was found to converge to the diffusion controlled value of 2.0 for all ϕ. In the absence of surfactant, that is for $\phi = 0$, our results were in agreement with those reported by Abramazon and Fishbein [29]. For $\phi > 0.1\pi$, significant reductions in Sherwood number were obtained. The extent of this mass transfer hindrance increases as a function of both ϕ and Peclet number. In Figs. 3–8 we present numerical results for the Sherwood number as a function of cap angle and Peclet number. We present results only for the case of $\kappa = 1.0$, i.e. the drop and the continuous phase viscosities are equal. Note however that the Sherwood number dependencies dis-

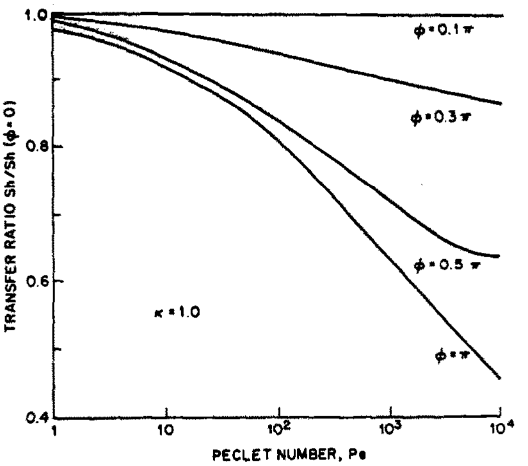

FIG. 4. Plot of the transfer ratio vs log Peclet number for $\phi = 0.1\pi$, 0.3π, 0.5π, and π for reduced convection.

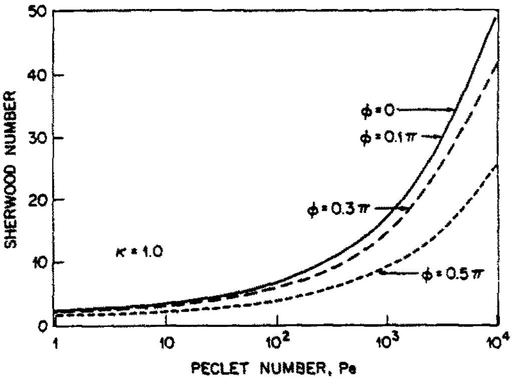

FIG. 5. Plot of the Sherwood number vs log Peclet number for $\phi = 0$, 0.1π, 0.3π, and 0.5π for surface blocking.

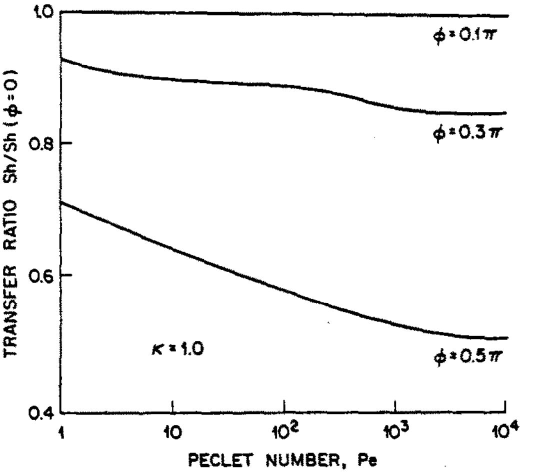

FIG. 6. Plot of the transverse ratio vs log Peclet number for $\phi = 0.1\pi$, 0.3π, and 0.5π for surface blocking.

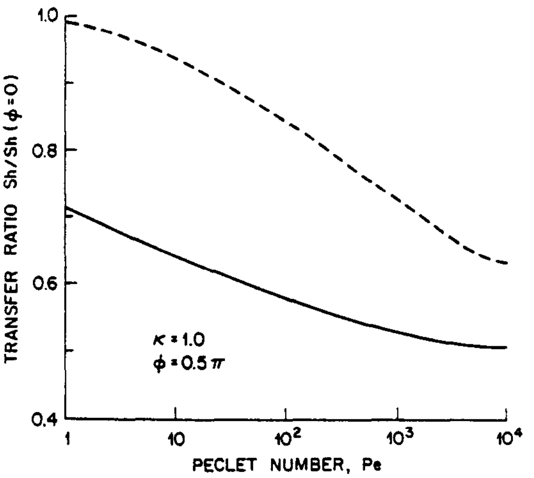

FIG. 7. Comparison of transfer ratio vs log Peclet number for reduced convection (dashed line) and for surface blocking (solid line) for a drop with $\phi = 0.5\pi$.

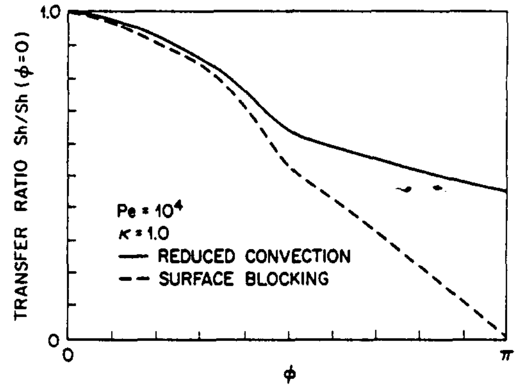

FIG. 8. Transfer ratios vs cap angle for reduced convection and for surface blocking for a Peclet number equal to 10^4.

cussed in the following paragraphs hold independent of finite κ value.

Sherwood number results for the case in which the adsorbed surfactant offers no resistance barrier to solute transport are given in Figs. 3 and 4. In this case, mass transfer hindrance relative to that for clean drop arises solely as a consequence of reduced convection. In Fig. 3, we have plotted the Sherwood number as a function of Peclet number for several values of ϕ. Maximum values of the Sherwood number are obtained in the absence of surface-active agents, i.e. $\phi = 0$. As the extent of the cap angle increases, the Sherwood number decreases. When the amount of adsorbed surfactant is small, i.e. $\phi = 0.1\pi$, virtually no mass transfer reduction is observed. Upon increasing the cap angle to 0.3π, significant reductions in mass transport efficiency relative to that for $\phi = 0$ are predicted. For fixed Peclet number, the maximum decrease in mass transport occurs when the drop is completely covered by surfactant. In this limit, $\phi = \pi$, the interfacial mobility of the drop tends to zero over the entire interface and consequently the drop settles as a solid sphere. The solid sphere behavior for $\phi = \pi$ is confirmed by the agreement of our calculated Sherwood numbers with the asymptotic values predicted from boundary layer analysis (that is $Sh \propto Pe^{1/3}$ [26]) for a Peclet number greater than 10^3. The maximum reductions in the solute mass transfer coefficient which can be attributed to the effect of reduced convection alone is given by the $\phi = \pi$ curve.

These results are summarized in Fig. 4 where we have plotted the Sherwood numbers normalized by the clean drop value, $Sh(\kappa, Pe; \phi = 0)$, as a function of the Peclet number. We refer to Sherwood numbers normalized in this fashion as the transfer ratio for a given Peclet number and ϕ. For fixed ϕ, mass transfer hindrance becomes more severe as the Peclet number increases due to the increasing relative importance of convection to diffusion as a mechanism of transport. For small cap angle, i.e. $\phi = 0.1\pi$, the transfer ratio is unity for all Peclet numbers; which suggests that negligible convective hindrance is produced when either surfactant adsorption is small or when surfactant is compressed to a small area. For higher surfactant coverage, the transfer ratios exhibit a significant Peclet number dependence. In the limit of full surface coverage, the transfer ratios are the minimum values which are attainable under the assumption that the surfactant presents no appreciable physical barrier to solute diffusion. Note that for $\phi = \pi$ and Peclet number equal to 10^4, we calculate the transfer ratio to be about 45%. This value is comparable in order of magnitude to the mass transfer coefficient reductions reported by Garner and Hale [3] for the case of solute mass transfer outside a sedimenting drop. However, there is no evidence that the distribution of *Teepol* in these experiments was one of full surface coverage, and thus we are unable to attribute the findings of Garner *et al.* to the hydrodynamics alone. It is, however, important to note that these results show that significant reductions in mass transfer can be attributed to reduced convection.

In Figs. 5 and 6, we show Sherwood number results for the case in which the adsorbed surfactant sterically hinders the passage of solute from the drop to the exterior phase. In this case, the Sherwood number results reflect the combined effect of surface blocking due to the physical barrier of the adsorbed surfactant monolayer as well as that of reduced convection. In Fig. 5 we have plotted *Sh* vs *Pe* for several values of the cap angle, ϕ. As noted previously in Fig. 3, the maximum amount of solute mass transfer occurs in the absence of contaminant, and the coincidence of the $\phi = 0.1\pi$ and 0.0 curves point to the fact that for low surface coverages no appreciable hindrance of mass transfer occurs. As the surface coverage increases to 30 and 50% of the total interfacial area, Sherwood number values are significantly reduced. We have replotted these results in Fig. 6, where the transfer ratios for $\phi = 0.1$, 0.3, and 0.5π are shown as a function of the Peclet number. For $\phi = 0.1\pi$, this ratio is one, independent of the Peclet number. For the larger cap angles, the transfer ratios are considerably less than unity even for low Peclet number. From the $\phi = 0.5\pi$ curve, we see that the transfer ratio is approximately 72% for a Peclet number equal to one. We can compare this value to the transfer ratio which was obtained based on the assumption of reduced hydrodynamics alone (see Fig. 4). From the reduced convection curve, we note that the calculated transfer ratio for Peclet number equal to one is 98% for $\phi = 0.5\pi$. The incorporation of the transfer resistance barrier via a zero flux condition on the stagnant cap demonstrates that the extent of mass transfer can be seriously overestimated if surface blocking is ignored.

In Fig. 7, we compare the Peclet number dependence of the mass transfer coefficients obtained in the case of full surface blocking with those obtained in the limit of reduced convection. The transfer ratios are plotted as a function of *Pe* for cap angle of 0.5π. On the upper curve, the reduced convection normalized transfer coefficients are plotted, while the lower curve corresponds to transport in the case of full surface blocking. The surface blocking transfer ratios are always lower than the corresponding reduced convection values, and in addition, they exhibit a weaker Peclet number dependence. For Peclet number equal to one, for example, the transfer ratio drops from 98% down to 72% when the effect of surface blocking is incorporated, whereas for Peclet number equal to 10^4, the transfer ratios are 67 and 54%, respectively. The Peclet number dependence can be understood as follows. As convection begins to dominate diffusion, i.e. $Pe \gg 1$, solute transport is determined primarily by hydrodynamics. In the presence of contaminants, the reduced interfacial velocity curtails transport via convection, an effect which becomes more acute for increasing Peclet number. The diminished sensitivity of the surface blocking Sherwood number to increasing *Pe*, reflects the fact that for systems in which the surfactant sterically obstructs the passage of solute, it is the hindered flux which largely determines the net interfacial transport rather than the local hydrodynamics.

In Fig. 8, we examine the cap angle dependence of the reduced convection and surface blocking transfer ratios for a Peclet number equal to 10^4. For small ϕ, the transport of solute is not appreciably hindered relative to clean drop transport values, and consequently the transfer ratio is unity for $\phi < 0.1\pi$. With increasing cap size, the Marangoni stress increases thereby reducing convective transport, as reflected by the drop off in the transfer ratio. Surface blocking does not significantly affect solute transport until the surface coverage exceeds 20%. For larger cap angles, steric impedance of solute transport leads to appreciable reductions in the calculated transfer ratios relative to the reduced convection values. Note that when $\phi = \pi$, the surface blocking boundary condition of zero flux yields the trivial solution of zero Sherwood number.

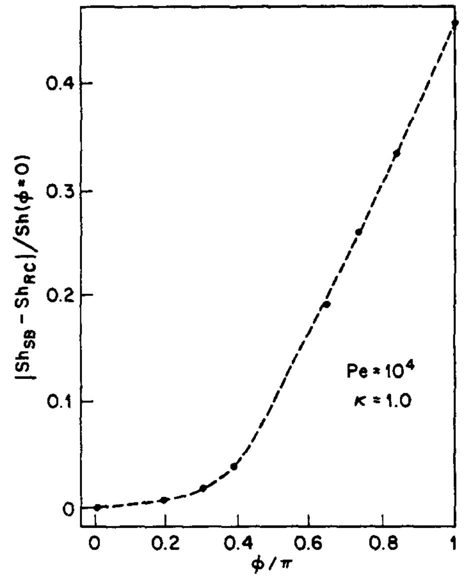

FIG. 9. The absolute Sherwood number difference vs ϕ for $Pe = 10^4$.

A comparison of the surface blocking transfer ratios with those calculated on the basis of stagnant cap hydrodynamics alone, show that the additional transfer hindrance reductions due to steric hindrance do not scale simply with percent surface coverage, ϕ. In Fig. 9, we plot the absolute difference between Sherwood numbers calculated under reduced convection and surface blocking boundary conditions, as a function of the contaminant covered surface area. In this manner, we isolate the excess hindrance which stems directly from steric blocking from that due to Marangoni reduced convection. A plot of this normalized Sherwood number difference for $Pe = 10^4$, suggests two distinct regimes. For $\phi > 0.4\pi$, the excess transport hindrance scales geometrically, i.e. linearly with ϕ. For smaller coverages, the steric hindrance has a weaker ϕ dependence. The importance of surface blocking can be underlined by comparing the maximum amount of transfer hindrance which can occur as a result of hydrodynamic considerations alone with transfer reductions predicted for the surface blocking case. At a Peclet number of 10^4 and $\phi = \pi$, a 45% transfer ratio was obtained. A comparable degree of transfer hindrance occurs for a drop with cap angle of 0.55π if the surface blocking effect is incorporated. Based on this fact, it is obvious that the mass transfer reductions reported by Garner and Hale [3] could equally well be explained on the basis of partial surfactant drop coverage and a full interfacial diffusion barrier. The relative contribution of reduced hydrodynamics and surface blocking to the mass transfer hindrances reported in this and other experiments will depend on the specifics of the surfactant adsorption behavior, conformation, and its physical–chemical interaction with the solute.

5. CONCLUSION

The Sherwood numbers for single-drop solute mass transport which we have calculated using the exterior stagnant cap velocities, indicate that significant mass transfer hindrance will result from the presence of trace amounts of surfactants. The large magnitude of the mass transfer reductions predicted by our simulation agree qualitatively with values determined in a number of experimental studies [3–5]. We have been able to show that for surface coverages greater than 0.1π, the contribution of surface blocking cannot be ignored. The effect of surface blocking becomes increasingly more important as the cap angle increases. For $\phi > 0.3\pi$, mass transfer coefficients calculated on the basis of reduced hydrodynamics alone may significantly overestimate the efficiency of a particular extraction process.

In this paper, we determined the Sherwood numbers for surface blocking under the assumption of complete impenetrability of the cap region. However, there may be a number of physical systems for which no interfacial surface barrier or merely a partial interfacial blocking will be produced by the presence of surfactants. As such, our calculated Sherwood numbers determine the upper limit for the mass transfer reductions which may occur in actual multiphase systems as a result of surface blocking. Nevertheless, the importance of understanding the potential effects of interfacial surface blocking as a factor which in conjunction with the appropriate hydrodynamics will determine the efficiency of industrial extraction processes is essential when the contaminant in question is a bulky molecule capable of steric blocking. In addition to the importance of this problem for chemical engineering applications, delineating the effect of contaminant surface blocking may be necessary for understanding a class of problems in the field of atmospheric science. The increasing presence of organic contaminants in the atmosphere has led to a concern on the part of some scientists that the adsorption and reaction of the organic acids on the surface of liquid-water cloud drops may alter the dynamics of atmospheric droplet evaporation [31]. Because of the organic component of these contaminants, these acids will be largely confined to the water drop–air interface. The potential for surface blocking of the water molecules which attempt to diffuse into or evaporate from these aqueous drops is evident. Mass transfer simulations which determine the effect of organic acids on the evaporation of liquid-water cloud droplets are greatly needed.

REFERENCES

1. R. Toossi and T. Novakov, The lifetime of aerosols in ambient air: considerations of the effects of surfactants and chemical reactions, *Atmos. Environ.* **19**, 127–133 (1985).
2. S. Schwartz. Mass-transport considerations pertinent to aqueous-phase reactions of gases in liquid-water clouds, presented at the NATO Advanced Study Institute on Chemistry of Multiphase Atmospheric Systems, Corfu, Greece (1983).
3. F. H. Garner and A. R. Hale, The effect of surface active agents in liquid extraction processes, *Chem. Engng Sci.* **2**, 157–163 (1953).
4. K. P. Lindland and S. G. Terjesen, The effect of a surface-active agent on mass transfer in falling drop extraction, *Chem. Engng Sci.* **5**, 1–12 (1956).
5. L. Mekasut, J. Molinier and H. Angelino, Effects of surfactants on mass transfer outside drops, *Chem. Engng Sci.* **33**, 821–829 (1978).
6. E. K. Rideal, On the influence of thin surface films on the evaporation of water, *J. Chem. Phys.* **29**, 1585–1588 (1925).
7. I. Langmuir and V. J. Schaefer, Rates of evaporation of water through compressed monolayers on water, *J. Franklin Inst.* **235**, 119–162 (1943).
8. R. J. Archer and V. La Mer, The rate of evaporation through fatty acid monolayers, *J. Phys. Chem.* **59**, 200–208 (1955).
9. R. E. Plevan and J. A. Quinn, The effect of monomolecular films on the rate of gas adsorption into a quiescent liquid, *A.I.Ch.E. Jl* **12**, 894–902 (1966).
10. J. C. Burnett and D. M. Himmelblau, The effect of surface active agents on interphase mass transfer, *A.I.Ch.E. Jl* **16**, 185–193 (1970).
11. L. K. Mudge and W. J. Heideger, The effect of surface active agents on liquid–liquid mass transfer rates, *A.I.Ch.E. Jl* **16**, 602–608 (1970).
12. W. S. Huang and R. C. Kintner, Effect of surfactants on mass transfer inside drops, *A.I.Ch.E. Jl* **15**, 735–744 (1969).
13. P. Savic, Circulation and distortion of liquid drops falling through a viscous medium, Natn. Res. Counc. Can. Div. Mech. Engrs Rep. MT-22 (1953).
14. F. H. Garner and A. H. P. Skelland, Some factors affecting droplet behavior in liquid–liquid systems, *Chem. Engng Sci.* **4**, 149–158 (1955).
15. E. R. Elzinga and J. T. Banchero, Some observations on the mechanics of drops in liquid–liquid systems, *A.I.Ch.E. Jl* **7**, 394–399 (1961).
16. R. M. Griffith, The effects of surfactants on the terminal velocity of drops and bubbles, *Chem. Engng Ser.* **17**, 1057–1070 (1962).
17. T. J. Horton, T. R. Fritsch and R. C. Kintner, Experimental determination of circulation velocities inside drops, *Can. J. Chem. Engng* **43**, 143 (1965).
18. A. Beitel and W. J. Heideger, Surfactant effects on mass transfer from drops subject to interfacial instability, *Chem. Engng Sci.* **26**, 711–717 (1971).
19. S. S. Sadhal and R. E. Johnson, Stokes flow past bubbles and drops partially coated with thin films. Part I. Stagnant cap of surfactant film—exact solution, *J. Fluid Mech.* **126**, 237–250 (1953).
20. V. G. Levich, *Physiochemical Hydrodynamics*, p. 390. Prentice-Hall, New York (1962).
21. R. E. Davis and A. Acrivos, The influence of surfactants on creeping motion of bubbles, *Chem. Engng Sci.* **21**, 681–685 (1966).
22. J. F. Harper, On bubbles with small immobile adsorbed films rising in liquids at low Reynolds number, *J. Fluid Mech.* **58**, 539–545 (1973).
23. J. F. Harper, Surface activity and bubble motion, *Appl. Scient. Res.* **38**, 343–352 (1982).
24. A. C. Lochiel, The influence of surfactants on mass transfer around spheres, *Can. J. Chem. Engng* **43**, 40–44 (1965).
25. P. A. Fox, A. D. Hall and N. L. Schryer, The PORT mathematical subroutine library, *TOMS* **4**, 104–126 (1978).
26. A. C. Lochiel and P. H. Calderbank, Mass transfer in the continuous phase around axisymmetric bodies of revolution, *Chem. Engng Sci.* **19**, 471–484 (1964).

27. N. L. Schryer, SSAF—Smooth Spline Approximations to Functions, AT&T Bell Laboratories Computer Science Technical Report No. 131 (1987).
28. O. C. Zienkiewicz, Finite element methods in thermal problems. In *Numerical Methods in Heat Transfer*. Wiley, New York (1981).
29. B. Abramazon and G. A. Fishbein, Some problem of convective diffusion to a spherical particle for $Pe \leqslant 1000$, *J. Engng Phys.* (*USSR*) **32,** 1053–1058 (1977).
30. P. S. Gill and T. E. Graedel, Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, rain drops, and snow flakes, *Rev. Geophys. Space Phys.* **21,** 903–920 (1983).

APPENDIX

The stream functions which describe the velocity in and around a stagnant cap drop are given by Sadhal and Johnson [19] as

$$\Psi(r,\theta) = \left(r^2 - \frac{1}{r}\right)\int_{\cos\theta}^{1} P_1(x)\,\mathrm{d}x + \sum_{k=1}^{\infty} C_k^*(r^{-k+2} - r^{-k})\int_{\cos\theta}^{1} P_k(x)\,\mathrm{d}x \quad \text{(A1)}$$

for the continuous phase and

$$\hat{\Psi}(r,\theta) = \frac{3}{2}(r^4 - r^2)\int_{\cos\theta}^{1} P_1(x)\,\mathrm{d}x + \sum_{k=1}^{\infty} C_k^*(r^{k+3} - r^{k+1})\int_{\cos\theta}^{1} P_k(x)\,\mathrm{d}x \quad \text{(A2)}$$

for the drop phase. Note that $P_k(x)$ is the kth order Legendre polynomial where $x = \cos\theta$. The coefficients C_1^* and C_k^* are given by

$$C_1^* = -\left\{\frac{\mu}{4\pi(\mu+\hat{\mu})}\left(2\phi + \sin\phi - \sin 2\phi - \frac{1}{3}\sin 3\phi\right) + \frac{2\mu + 3\hat{\mu}}{2(\mu+\hat{\mu})}\right\} \quad \text{(A3)}$$

and

$$C_k^* = \frac{\mu}{4\pi(\mu+\hat{\mu})}\left\{\sin(k+2)\phi - \sin k\phi + \sin(k+1)\phi - \sin(k-1)\phi - 2\left[\sin\frac{(k+2)\phi}{(k+2)} + \sin\frac{(k-1)\phi}{(k-1)}\right]\right\} \quad \text{(A4)}$$

where μ and $\hat{\mu}$ are the exterior and drop phase viscosities, respectively.

The terminal velocity of the stagnant cap drop U_s, is

$$U_s = \left\{\frac{\frac{3}{2}U_{\text{STOKES}}}{\frac{\mu}{4\pi(\mu+\hat{\mu})}\left(2\phi + \sin\phi - \sin 2\phi - \frac{1}{3}\sin 3\phi\right) + \frac{2\mu+3\hat{\mu}}{2(\mu+\hat{\mu})}}\right\}. \quad \text{(A5)}$$

L'EFFET DU BLOCAGE DE SURFACE SUR LE TRANSFERT DE MASSE A PARTIR D'UNE GOUTTE

Résumé—On présente des résultats numériques pour le transfert de masse de soluté à partir d'une goutte unique couverte par un surfactant. En particulier, on détermine l'effet de blocage physicochimique de la surface dans le cas ou le surfactant absorbé s'accumule à l'arrière de la goutte en translation. Le blocage de la surface est intégré dans le choix d'une condition limite de flux nul sur les portions de la goutte où le surfactant est présent. Des résultats numériques obtenus par les éléments finis pour le nombre de Sherwood en fonction du nombre de Peclet ($Pe \leqslant 10^4$), avec un angle au sommet stagnant ϕ, montrent que pour une surface supérieure à $0{,}1\pi$ l'effet du blocage de la surface ne peut être ignoré. Pour un nombre de Peclet égal à 10^4 et $\phi = 0{,}5\pi$, les coefficients de transfert de masse, calculés avec l'hypothèse d'un surfactant réduisant la convection au voisinage de la goutte sans inhiber le transfert interfacial de soluté, sont surestimés de 20% environ.

EINFLUSS DER OBERFLÄCHENBLOCKIERUNG AUF DEN STOFFÜBERGANG AN EINEM TROPFEN MIT INAKTIVER OBERFLÄCHE

Zusammenfassung—Für den Stoffübergang an einem einzelnen Tropfen, der mit einer oberflächenaktiven Substanz bedeckt ist, werden numerische Ergebnisse vorgestellt. Insbesondere wird der Einfluß einer physiko-chemischen Oberflächenblockierung bestimmt. Dabei wird ein fallender Tropfen betrachtet, bei dem sich der absorbierte oberflächenaktive Stoff oben auf dem fallenden Tropfen ansammelt. Das Geschwindigkeitsprofil im inaktiven Bereich wird zur Beschreibung des konvektiven Transports verwendet. Die Oberflächenblockierung wird durch die Wahl einer Randbedingungen dargestellt, die keinen Stofftransport in denjenigen Bereichen des Tropfens zuläßt, in welchen der oberflächenaktive Stoff vorhanden ist. Ergebnisse der Finite-Elemente-Berechnung liegen für Sherwood-Zahlen als Funktion der Peclet-Zahl ($Pe \leqslant 10^4$) und des Winkels ϕ der inaktiven Oberfläche vor. Bei einer Oberflächenbedeckung von mehr als $0{,}1\pi$ darf die Oberflächenblockierung nicht vernachlässigt werden. Für eine Peclet-Zahl von 10^4 und $\phi = 0{,}5\pi$ werden die Stoffübergangskoeffizienten unter der Annahme berechnet, daß der oberflächenaktive Stoff die Konvektion in der Nähe des Tropfens verringert, ohne jedoch den Stofftransport an der Phasengrenze zu verhindern. Dabei wird der Stofftransport um 20% zu hoch berechnet.

ВЛИЯНИЕ БЛОКАДЫ ПОВЕРХНОСТИ НА МАССОПЕРЕНОС В ЗАСТОЙНОЙ ЗОНЕ КАПЛИ

Аннотация—Представлены численные результаты по переносу массы от внешней, покрытой ПАВ поверхности единичной капли раствора в непрерывную фазу. В частности, эффект блокады поверхности определяется физико-химическими процессами при накоплении поглощаемого ПАВ в кормовой части перемещающейся капли. Для описамия конвективного переноса используются профили скоростей в застойной зоне. Блокада поверхности дополняется граничным условием нулевого потока массы на частях капли с ПАВ. Численные результаты, полученные методом конечных элементов для чисел Шервуда в зависимости от значений числа Пекле ($Pe \leqslant 10^4$) и угла застойной зоны ϕ показывают, что в случае, если больше чем $0,1\pi$ поверхности покрыто ПАВ, эффектом блокады поверхности нельзя пренебрегать. Найдено, что при значении числа Пекле до 10^4 и $\phi = 0,5$ коэффициенты массопереноса, рассчитанные в предположении, что наличие ПАВ уменьшает конвекцию вблизи капли без подавления межфазного переноса растворенного вещества, завышают скорость переноса его массы на 20%.