y = distance transverse to flow
γ = wall-shear rate
λ_n = eigenvalue
$<\psi>$ = dimensionless mixing cup solute concentration
ϕ = volume fraction of particles

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The Effect of Surfactant on the Terminal and Interfacial Velocities of a Bubble or Drop

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Stream functions are derived for a spherical droplet in creeping flow with an arbitrary surface tension gradient at its interface. The stream functions are used to show theoretically that the terminal velocity is reduced and that the interfacial velocity is retarded, especially near the rear of the droplet, when a trace of surfactant is present in the exterior phase and when surface aging is controlled by diffusion.

SCOPE

Experimental investigations of droplet motion in liquid containing a surface active impurity have shown that, compared to motion in pure liquid, both the terminal velocity and the interfacial velocity of a droplet are reduced, the latter particularly near the rear of the droplet.

Here a theoretical investigation of droplet motion in systems contaminated by surfactant is presented. The ob-

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jectives of the study are to obtain relations for the terminal velocity and the interfacial velocity of a droplet in creeping flow with a variation of surface tension at its interface and to show that these relations are consistent with experimental results.

Besides providing a theoretical framework for droplet motion in contaminated systems, this work contributes to a knowledge of the behavior of mobile interfaces which is important for the optimal design and operation of vessels in which mass transfer or phase separation take place.

CONCLUSIONS AND SIGNIFICANCE

Equations for the terminal velocity and the interfacial velocity are derived for a droplet with an arbitrary surface tension gradient at its interface caused by surfactant present in either or in both phases. It is assumed that the droplet is spherical, that it has reached its terminal velocity, that inertial terms in the equations of motion are negligible, and that viscosities and densities are not functions of local surfactant concentration. An example is given with surface aging controlled by diffusion in the exterior phase to show theoretically that the presence of surfactant causes a decrease in both the terminal velocity and the interfacial velocity. Furthermore, the interfacial velocity near the rear of the droplet is found to be extremely sensitive to surfactant concentration.

The relations presented for the terminal velocity and the interfacial velocity are consistent with experimental observation and have not been previously reported.

Mobile interfaces are encountered frequently in industrial operations. Since industrial liquids are rarely pure, surface-active impurities can accumulate at an interface and, if surface tension gradients result, change the hydrodynamic behavior of a system. This in turn may reduce convective mass transfer rates and reduce the efficiency of a contacting device.

To understand better the effects of surfactant on the motion of mobile interfaces, we consider here a single droplet creeping through a liquid phase. Either one or both of the phases contain surfactant which is adsorbed at the interface and is swept toward the rear of the droplet by the fluid motion. The concentration of surfactant reaches a maximum at the rear stagnation point. The resulting surface tension gradient retards the velocity of the interface, particularly near the rear of the droplet, and reduces the terminal velocity of the droplet.

In this paper, the stream functions for the droplet and exterior phases are derived for a spherical droplet in creeping flow with an arbitrary surface tension gradient at its interface. From the stream functions, equations for the terminal velocity and for the interfacial velocity of the droplet are obtained. Following the derivation, an example is given, with surface aging controlled by diffusion in the exterior phase, to show that the derived relations are consistent with experimental observations reported in the literature.

BACKGROUND

Equations for the motion of a droplet, derived by Hadamard and Rybczyński and reviewed by Levich (1962), give streamlines which are symmetric about the equator of the droplet. Failure of the Hadamard-Rybczyński formulation to agree with experimentally measured terminal velocities led Levich to propose that surfactants accumulate near the rear of a droplet and that the resulting surface tension gradient retards the motion of the interface and decreases the terminal velocity of the droplet. He obtained solutions for surface aging controlled by diffusion in the bulk, surface diffusion, and adsorption kinetics (see also Newman, 1967). Because of assumptions made in the theoretical analysis, including the use of a constant thickness for the Nernst diffusion layer, the streamlines are again symmetric about the equator of the droplet.

Photographs of water drops falling through castor oil, taken by Savic (1953), indicate that streamlines are not symmetric about the equator of a drop. In fact, the velocity of the interface appears to vanish near the rear stagnation point, forming a stagnant cap over the rear of a drop. Similar observations have been reported by Garner and Skelland (1955), Elzinga and Banchero (1961), Horton et al. (1965), and Beitel and Heideger (1971). Surfactants are responsible for this behavior, as shown experimentally by Griffith (1962).

With an assumed form for the surface tension gradient, Schechter and Farley (1963) solved the equations of motion for a droplet in creeping flow. As a result of using a normal force balance for a boundary condition, they concluded that the assumed form for the surface tension gradient was the only form consistent with the assumption of a spherical droplet. However, they also showed that the assumed form reduces velocities uniformly everywhere rather than predominately near the rear of the droplet.

Wasserman and Slattery (1969) solved the governing differential equations for a trace of surfactant present in the exterior phase and surface aging controlled by diffusion. In obtaining an approximate solution to the convective diffusion equation by Galerkin's method, their perturbation approach permitted them to use velocity components from the Hadamard-Rybczyński formulation for droplet motion in a pure fluid. Thus, their results are useful only in the region where the interfacial velocity is not retarded significantly.

For information on droplet motion in general, Harper (1972) has written a comprehensive review article.

THEORY

To begin our derivation of the stream functions, we consider a spherical droplet of radius R held stationary in space by liquid flowing slowly past it at a velocity approaching U far from the droplet. Either one or both of the phases contain surfactant. The viscosities and densities are assumed not to be functions of local surfactant concentration. Inertial forces are assumed to be negligible compared to viscous forces. Properties of the droplet phase are denoted by a carat. The radial coordinate r is measured from the center of the droplet. The angle θ is measured from the front stagnation point. Local velocities are determined by differentiating the stream function:

$$v_r = -\frac{1}{r^2 \sin\theta}\frac{\partial\psi}{\partial\theta} \qquad (1)$$

$$v_\theta = \frac{1}{r \sin\theta}\frac{\partial\psi}{\partial r} \qquad (2)$$

The differential equations for the system are

$$E^2(E^2\psi) = 0 \tag{3}$$

$$E^2(E^2\hat{\psi}) = 0 \tag{4}$$

where

$$E^2 = \frac{\partial^2}{\partial r^2} + \frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\right)$$

In the exterior phase, the boundary conditions are

$$\psi \to \frac{U}{2} r^2 \sin^2\theta \quad \text{as} \quad r \to \infty \tag{5}$$

$$v_r = 0 \quad \text{at} \quad r = R \tag{6}$$

The first boundary condition describes uniform streaming at infinity. The second requires the normal velocity to vanish at the interface.

The boundary conditions for the droplet phase are

$$\hat{v}_r \text{ and } \hat{v}_\theta \text{ are bounded at } r = 0 \tag{7}$$

$$\hat{v}_r = 0 \quad \text{at} \quad r = R \tag{8}$$

In addition to the boundary conditions for each phase, the differential equations are coupled by two boundary conditions applied at the interface:

$$v_\theta = \hat{v}_\theta \quad \text{at} \quad r = R \tag{9}$$

$$\frac{1}{R}\frac{d\sigma}{d\theta} = \tau_{r\theta} - \hat{\tau}_{r\theta} \quad \text{at} \quad r = R \tag{10}$$

The first of these boundary conditions requires the tangential velocities to be continuous. The last boundary condition is a tangential force balance, where $d\sigma/d\theta$ is the surface tension gradient.

The general solution to Equations (3) and (4) has been discussed in detail by Happel and Brenner (1965). For the problem posed here, the appropriate forms are

$$\psi = \sum_{n=2}^{\infty} (A_n r^n + B_n r^{-n+1} + C_n r^{n+2} + D_n r^{-n+3}) C_n^{-1/2}(\cos\theta) \tag{11}$$

$$\hat{\psi} = \sum_{n=2}^{\infty} (\hat{A}_n r^n + \hat{B}_n r^{-n+1} + \hat{C}_n r^{n+2} + \hat{D}_n r^{-n+3}) C_n^{-1/2}(\cos\theta) \tag{12}$$

where $C_n^{-1/2}$ $(\cos\theta)$ is the Gegenbauer polynomial of order n and degree $-\frac{1}{2}$.

The Gegenbauer polynomials of degree $-\frac{1}{2}$ are related to Legendre functions. They have been discussed by Savic (1953), Haberman and Sayre (1958), Happel and Brenner (1965), and Wasserman and Slattery (1969). The even-order polynomials are symmetric about the equator, and the odd-order ones are antisymmetric. The first polynomial of our series is

$$C_2^{-1/2}(\cos\theta) = \frac{\sin^2\theta}{2} \tag{13}$$

The orthogonal property of the Gegenbauer polynomials is

$$\int_0^\pi \frac{C_m^{-1/2}(\cos\theta) C_n^{-1/2}(\cos\theta)}{\sin\theta} d\theta = \begin{cases} 0 & \text{for} \quad m \neq n \\ \dfrac{2}{n(n-1)(2n-1)} & \text{for} \quad m = n \end{cases} \tag{14}$$

The boundary conditions for the exterior phase are applied to Equation (11) in a straightforward manner. Using the first boundary condition, Equation (5), we obtain

$$A_2 = U \tag{15}$$

$$A_n = 0 \quad \text{for} \quad n > 2 \tag{16}$$

$$C_n = 0 \quad \text{for all} \quad n \tag{17}$$

The second boundary condition, Equation (6), gives relations among the coefficients:

$$D_2 = -UR - B_2 R^{-2} \tag{18}$$

$$D_n = -B_n R^{-2} \quad \text{for} \quad n > 2 \tag{19}$$

These are used to eliminate D_n from Equation (11), giving

$$\psi = \frac{U}{2}(r^2 - Rr)\sin^2\theta - \sum_{n=2}^{\infty} B_n(R^{-2} r^{-n+3} - r^{-n+1}) C_n^{-1/2}(\cos\theta) \tag{20}$$

The boundary conditions for the droplet phase can be applied to Equation (12) in a similar way to give

$$\hat{\psi} = \sum_{n=2}^{\infty} \hat{A}_n (r^n - R^{-2} r^{n+2}) C_n^{-1/2}(\cos\theta) \tag{21}$$

The stream functions are now differentiated to determine tangential velocities, and Equation (9) is used. Coefficients multiplying the Gegenbauer polynomials are equated, giving the relations

$$\hat{A}_2 = \frac{-U}{2} + B_2 R^{-3} \tag{22}$$

$$\hat{A}_n = B_n R^{-2n+1} \quad \text{for} \quad n > 2 \tag{23}$$

These equations are used to eliminate $\hat{A}_n$ from the analysis.

It remains only to determine B_n. When the necessary differentiations have been performed, the last boundary condition, Equation (10), becomes

$$\frac{d\sigma}{d\theta} = \frac{3}{2} U \hat{\mu} \sin\theta - \frac{\mu + \hat{\mu}}{\sin\theta} \sum_{n=2}^{\infty} (4n - 2) B_n R^{-n-1} C_n^{-1/2}(\cos\theta) \tag{24}$$

To use the orthogonality relation, Equation (14), both sides of Equation (24) are multiplied by $C_m^{-1/2}$ $(\cos\theta)$ and integrated over θ from 0 to π. Rearrangement gives

$$B_2 = \frac{R^3}{\mu + \hat{\mu}}\left(\frac{U\hat{\mu}}{2} - \frac{1}{4}\int_0^\pi \sin^2\theta \frac{d\sigma}{d\theta} d\theta\right) \tag{25}$$

$$B_n = \frac{-n(n-1)}{4}\frac{R^{n+1}}{\mu + \hat{\mu}}\int_0^\pi C_n^{-1/2}(\cos\theta)\frac{d\sigma}{d\theta} d\theta \quad \text{for} \quad n > 2 \tag{26}$$

This completes the derivation of the stream functions.

They are

$$\psi = \frac{U}{4}\left(2 - \frac{2\mu + 3\hat{\mu}}{\mu + \hat{\mu}}\frac{R}{r} + \frac{\hat{\mu}}{\mu + \hat{\mu}}\frac{R^3}{r^3}\right) r^2 \sin^2\theta$$

$$+ \frac{1}{4}\frac{r^2 - R^2}{\mu + \hat{\mu}} \sum_{n=2}^{\infty} n(n-1) \times$$

$$\left[\int_0^{\pi} C_n^{-1/2}(\cos\theta)\frac{d\sigma}{d\theta}\,d\theta\right]\frac{R^{n-1}}{r^{n-1}} C_n^{-1/2}(\cos\theta) \tag{27}$$

$$\hat{\psi} = \frac{-U}{4}\frac{\mu}{\mu + \hat{\mu}}\left(1 - \frac{r^2}{R^2}\right) r^2 \sin^2\theta$$

$$- \frac{1}{4}\frac{R^2 - r^2}{\mu + \hat{\mu}} \sum_{n=2}^{\infty} n(n-1) \times$$

$$\left[\int_0^{\pi} C_n^{-1/2}(\cos\theta)\frac{d\sigma}{d\theta}\,d\theta\right]\frac{r^n}{R^n} C_n^{-1/2}(\cos\theta) \tag{28}$$

The velocity of the interface can be calculated from either stream function:

$$v_i = \frac{U}{2}\frac{\mu}{\mu + \hat{\mu}}\sin\theta + \frac{1}{2(\mu + \hat{\mu})}\sum_{n=2}^{\infty} n(n-1) \times$$

$$\left[\int_0^{\pi} C_n^{-1/2}(\cos\theta)\frac{d\sigma}{d\theta}\,d\theta\right]\frac{C_n^{-1/2}(\cos\theta)}{\sin\theta} \tag{29}$$

The terminal velocity is determined by the forces acting on the droplet. Following Haberman and Sayre, the drag force on the droplet is given by

$$F_d = -4\pi\mu D_2 \tag{30}$$

where D_2 is given by Equation (18). The drag force is balanced by the buoyant force:

$$F_b = \frac{4}{3}\pi R^3 g\,|\Delta\rho| \tag{31}$$

Equating the two forces and rearranging, we get the terminal velocity of the droplet:

$$U = \frac{2\mu + 2\hat{\mu}}{2\mu + 3\hat{\mu}}\left(\frac{R^2 g\,|\Delta\rho|}{3\mu}\right) + \frac{1}{4\mu + 6\hat{\mu}}\int_0^{\pi} \sin^2\theta\,\frac{d\sigma}{d\theta}\,d\theta \tag{32}$$

In certain cases, the equations derived here simplify to previously known relations. If the surface tension gradient is zero, the equations are those obtained by Hadamard and Rybczyński for droplet motion in a pure fluid. Furthermore, as $\hat{\mu}$ approaches infinity, the stream function for the droplet vanishes, indicating no internal circulation, and the stream function for the exterior phase is that for Stokes flow.

The equations in this section are not restricted to a trace of surfactant. Either one or both of the phases may contain enough surfactant to retard significantly the motion of the interface. We have assumed that the droplet is spherical, that it has reached its terminal velocity, that inertial forces are negligible, and that viscosities and densities are not functions of local surfactant concentration.

EXAMPLE

To demonstrate the behavior of the equations, an example, originally posed by Wasserman and Slattery, is given here. Their purpose was to predict the terminal velocity. We determine how a trace of surfactant perturbs both the terminal velocity and the velocity of the interface.

Consider a bubble ($\hat{\mu} = 0$, $\hat{\rho} = 0$) rising through a liquid at its steady state or terminal velocity. A trace of nonionic surfactant is presented in the liquid. The bulk region extends to infinity, where the concentration of surfactant is c_∞. Surface aging is assumed to be controlled by diffusion in the bulk.

Following Gibbs (1878), the interface is treated as a discontinuity. The concentration of surfactant in the interface is given the symbol Γ. Equilibrium between the interface and the liquid adjacent to it is described by the Gibbs adsorption isotherm with the activity coefficient equal to unity:

$$\Gamma = \frac{-c_i}{\mathcal{R}T}\frac{d\sigma}{dc_i} \tag{33}$$

Since only a trace of surfactant is present, the equilibrium is linear:

$$\Gamma = Kc_i \tag{34}$$

Diffusion of surfactant to and from the interface is described by the convective diffusion equation:

$$v_r\frac{\partial c}{\partial r} + \frac{v_\theta}{r}\frac{\partial c}{\partial\theta} = \frac{\mathcal{D}}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right)\right.$$

$$\left. + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial c}{\partial\theta}\right)\right] \tag{35}$$

The boundary conditions for Equation (35) are

$$c \to c_\infty \quad \text{as} \quad r \to \infty \tag{36}$$

$$\partial c/\partial\theta = 0 \quad \text{at} \quad \theta = 0 \tag{37}$$

$$\partial c/\partial\theta = 0 \quad \text{at} \quad \theta = \pi \tag{38}$$

$$\mathcal{D}\frac{\partial c}{\partial r} = \frac{1}{R\sin\theta}\frac{d(\Gamma v_i \sin\theta)}{d\theta} \quad \text{at} \quad r = R \tag{39}$$

The last boundary condition (Levich, 1962) equates the flux of surfactant to the interface to the divergence of the flux within the interface. Therefore, at any point the surfactant which diffuses to the interface is convected by the motion of the interface.

Since only a trace of surfactant is present in the liquid, to a first approximation the velocities are those for a bubble rising through pure liquid. Thus, v_r and v_θ from the Hadamard-Rybczyński analysis are substituted into Equation (35), which is then made dimensionless. In doing so, the following groups are formed:

$$c^* = \frac{c}{c_\infty} \qquad r^* = \frac{r}{R} \tag{40), (41}$$

$$Pe = \frac{2RU_O}{\mathcal{D}} \qquad K^* = \frac{K}{2R} \tag{42), (43}$$

The dimensionless differential equation was solved numerically by finite differences. Before doing so, however, it was necessary to choose numerical values for the parameters which appear in the equation and boundary conditions. Wasserman and Slattery chose numerical values for a hypothetical bubble rising through water containing a trace of isoamyl alcohol. To compare our results with theirs, we use the same values in this example:

T = 15°C $\quad$ $\mathcal{D} = 1.25 \times 10^{-6}$ cm²/s
$R = 1.095 \times 10^{-3}$ cm $\quad$ μ = 1.140 cp
ρ = 1.00 g/cm³ $\quad$ $K = 4.37 \times 10^{-5}$ cm

These values correspond to a terminal velocity U_O of 3.43

$\times 10^{-2}$ cm/s and a Reynolds number based on bubble diameter of 6.60×10^{-3}. Numerical values for the parameters appearing in the dimensionless differential equation and boundary conditions are $Pe = 60$ and $K^* = 0.02$.

In solving the differential equation numerically, the substitution $y \equiv \ln r^*$ was made to stretch the radial coordinate near the interface. The differential equation and boundary conditions were put into central difference form. The first boundary condition was applied by setting $c^* = 1$ at $y = 1$ for all θ. Application of this boundary condition further from the sphere gave essentially the same results. Convergence was obtained by using a matrix of concentrations with eighty-one equally spaced points in the y direction from $y = 0$ to $y = 1$ and eighty-one equally spaced points in θ direction from $\theta = 0$ to $\theta = \pi$.

The solution to the equation is shown graphically in Figure 1 in terms of the surfactant concentration adjacent to the interface and its gradient. The surfactant concentration is a minimum at the front stagnation point and a maximum at the rear stagnation point. The gradient is skewed dramatically towards the rear of the bubble. The radial concentration gradient at the interface, $\partial c^*/\partial r$ at $r = R$, changes sign at $\theta = 95$ deg. Thus, as the interface is compressed by the fluid motion over the rear half of the bubble, the interfacial concentration of surfactant rises, and surfactant diffuses away from the bubble.

The hydrodynamic results of this example can be expressed as the ratio of terminal velocity U to the terminal velocity predicted by the Hadamard-Rybczynski analysis U_O and the ratio of interfacial velocity v_i to the interfacial velocity predicted by the Hadamard-Rybczynski analysis v_{iO}. Equations (29), (32), (33), (34), and (40) can be combined to give these ratios in the forms

$$\frac{U}{U_O} = 1 - \kappa c_\infty \tag{44}$$

$$\frac{v_i}{v_{iO}} = 1 - \beta(\theta) c_\infty \tag{45}$$

with

$$\kappa = \frac{K\mathfrak{R}T}{4U_O\mu} \int_0^\pi \sin^2\theta \frac{dc_i^*}{d\theta} d\theta \tag{46}$$

$$\beta(\theta) = \kappa + \frac{K\mathfrak{R}T}{U_O\mu} \sum_{n=2}^{\infty} n(n-1) \times \left[\int_0^\pi C_n^{-1/2}(\cos\theta) \frac{dc_i^*}{d\theta} d\theta\right] \frac{C_n^{-1/2}(\cos\theta)}{\sin^2\theta} \tag{47}$$

The integrals in κ and $\beta(\theta)$ were evaluated by using an extended Simpson integration. For the terminal velocity, a value of κ equal to 1.9×10^8 cm^3/mole was obtained. This compares well with the value of 2×10^8 cm^3/mole obtained by Wasserman and Slattery. The function β is plotted in Figure 2. Approximately twenty terms of the series were required for convergence. Note that the interfacial velocity is retarded much more near the rear of the bubble than it is over the front half. Also, since β near the rear of the bubble is much larger than κ, the interfacial velocity there is much more sensitive to surfactant concentration than is the terminal velocity.

To assess the magnitude of the reduction in the velocities, let the liquid contain 5×10^{-8} mole/l of isoamyl alcohol. This concentration would reduce the terminal velocity by 1% and the interfacial velocity near the rear stagnation point by more than 10%. Furthermore, the interfacial concentration of isoamyl alcohol at the rear stagnation point would be only 1 molecule/5×10^6 Å^2. This should be compared with the 20 Å^2 typically covered by a molecule in a condensed monomolecular film. In addition, the drop in surface tension from the front stagnation point to the rear stagnation point would be less than 4×10^{-5} dyne/cm.

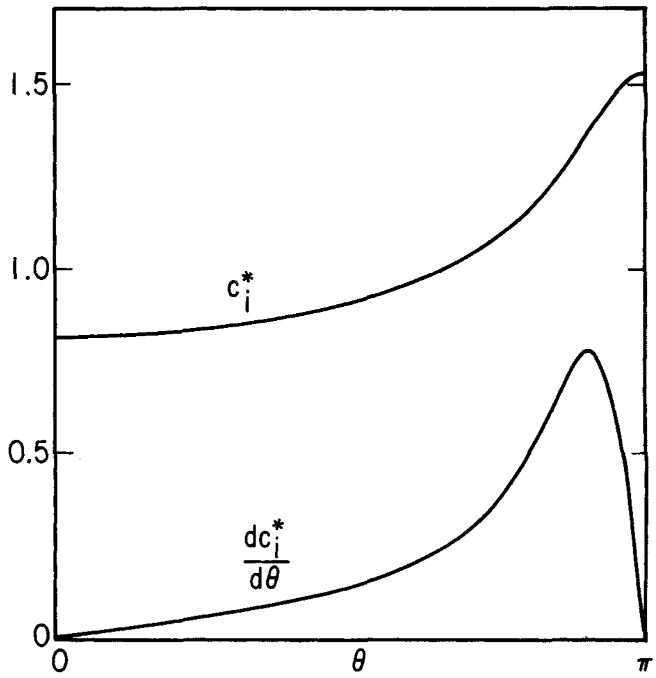

Fig. 1. Interfacial surfactant concentration and its gradient.

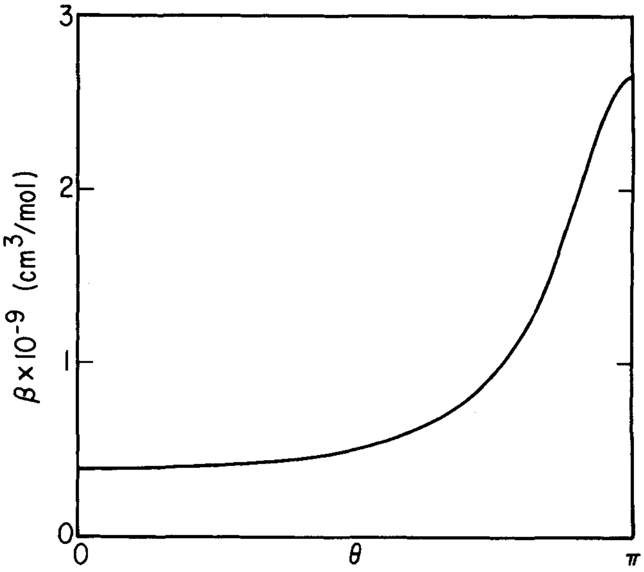

Fig. 2. Interfacial velocity function $\beta(\theta)$.

DISCUSSION

In studying the effect of surfactant on the motion of a droplet, the droplet has been assumed to be spherical. Normal forces acting on the interface will tend to deform the droplet from a spherical shape for two reasons. First, the inertial terms in the equations of motion have been neglected. For a droplet moving at low Reynolds number in a surfactant free system, the deformation caused by inertial forces acting on the interface has been analyzed by Taylor and Acrivos (1964). They found the deformation to be proportional to the Weber number for a slightly deformed droplet. From their results, for the bubble considered in the example, the ratio of the maximum deviation from sphericity to the effective radius of the bubble would be approximately 10^{-9}. Second, the droplet will be deformed because the surface tension in the normal force balance is not constant since it depends on the local interfacial surfactant concentration. However, when the variation of surface tension is small compared to its average value, the droplet will be essentially spherical. In fact, in experimental studies of droplet shape in contaminated systems, small droplets have always been observed to be spherical. Haberman and Morton (1956) found that bubbles in unpurified water are not deformed noticeably from a spherical shape below Reynolds numbers of 400. Since our stream functions are valid only up to Reynolds numbers of order unity, the deformation in this flow regime will be negligible for most droplets.

A small droplet in a contaminated system has been observed in several experimental studies to move at a terminal velocity corresponding to a rigid interface. Schechter and Farley derived the surface tension gradient which is necessary to stop the interface of a droplet:

$$\frac{d\sigma}{d\theta} = \frac{-R^2 g|\Delta\rho|}{3}\sin\theta \qquad (48)$$

Equations (29) and (32) can be used to verify this result. Also, by integrating Equation (48), it can be shown that for the bubble considered in the example, the interface would stop if the surface tension at the rear stagnation point were only 8×10^{-4} dyne/cm less than that at the front stagnation point.

Several investigators have attempted to solve approximately the problem of surface aging controlled by diffusion in the bulk. As mentioned previously, Levich assumed a constant thickness for the Nernst diffusion layer. This thickness is of the form

$$\delta \equiv \frac{c_\infty - c_i}{\partial c/\partial r|_{r=R}} \qquad (49)$$

When the numerical values from our example are substituted into this equation, we find that δ is discontinuous at $\theta = 95$ deg., where $\partial c/\partial r|_{r=R} = 0$. Also, since c_i is less than c_∞ until $\theta = 117$ deg., δ is negative between $\theta = 95$ and $\theta = 117$ deg. Therefore, it appears that the thickness of the Nernst diffusion layer has little if any significance in this problem because the interfacial concentration of surfactant varies with position.

It is also interesting to note that a boundary-layer approach to diffusion, discussed by Saville (1973) and by Harper (1974), would not result in reasonable interfacial velocities. Boundary-layer methods characteristically neglect diffusion in the θ direction. If such an approach had been implemented here, the boundary condition along the rear axis, Equation (38), could not have been satisfied. Consequently, near the rear of the droplet the concentration of surfactant would be unrealistically large and interfacial velocities excessively retarded.

We have adopted a numerical approach to the mass transfer problem in order to satisfy all of the boundary conditions. The interfacial concentration gradient which resulted from the analysis is reasonable, and the series for $\beta(\theta)$ converged without difficulty. We have been able to show that the terminal velocity is reduced if surfactant is present and that the interfacial velocity near the rear stagnation point is extremely sensitive to surfactant concentration. These results are consistent with experimental observation.

In the example, we have treated the case of an infinitely dilute solution of surfactant. For more concentrated systems, the mass transfer and fluid mechanics problems are coupled. One must find the surface tension gradient corresponding to the velocity field which gives the concentration distribution corresponding to the surface tension gradient.

NOTATION

A_n, B_n, C_n, D_n = constants appearing in Equation (11)
c = concentration of surfactant (mole/volume)
c^* = dimensionless concentration of surfactant defined by Equation (40)
c_i = concentration of surfactant in equilbrium with Γ
c_∞ = concentration of surfactant far from droplet
$C_n^{-1/2}(\cos\theta)$ = Gegenbauer polynomial of order n, degree $-\frac{1}{2}$, and argument $\cos\theta$
$\mathfrak{D}$ = diffusion coefficient
F_b = buoyant force defined by Equation (31)
F_d = drag force defined by Equation (30)
g = gravitational acceleration
K = adsorption coefficient
K^* = dimensionless adsorption coefficient defined by Equation (43)
m, n = summation indexes
Pe = Peclet number defined by Equation (42)
r = radial coordinate measured from center of droplet
r^* = dimensionless radial coordinate defined by Equation (41)
R = radius of droplet
$\mathfrak{R}$ = gas constant
T = absolute temperature
U = terminal velocity of droplet
U_O = terminal velocity of droplet in surfactant free system
v_i = interfacial velocity
v_{iO} = interfacial velocity in surfactant free system
v_r = velocity in radial direction
v_θ = velocity in θ direction
y = $\ln r^*$

Greek Letters

$\beta(\theta)$ = interfacial velocity function defined by Equation (47)
Γ = interfacial concentration of surfactant (mole/area)
δ = thickness of Nernst diffusion layer
θ = angle measured from front stagnation point
κ = terminal velocity parameter defined by Equation (46)
μ = viscosity
ρ = density
σ = surface tension
$\tau_{r\theta}$ = tangential shear stress, $-\mu[r\partial(v_\theta/r)/\partial r + (1/r)(\partial v_r/\partial\theta)]$
ψ = stream function
$\wedge$ = property of droplet phase

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A Lumping and Reaction Scheme for Catalytic Cracking

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A predictive kinetic model has been developed for fluid catalytic cracking (FCC). The kinetic scheme involves lumped species consisting of paraffins, naphthenes, aromatic rings, and aromatic substituent groups in light and heavy fuel oil fractions. The kinetic model also incorporates the effect of nitrogen poisoning, aromatic ring adsorption, and time dependent catalyst decay. The rate constants for these lumped species are invariant with respect to charge stock composition. The predictive capabilities of the model have been verified for wide ranges of charge stocks and process conditions.

SCOPE

The purpose of this work was to develop a predictive kinetic description of fluid catalytic cracking (FCC) for incorporation into an integrated FCC process model. Process models are useful for the design, optimization, and control of commercial plants. In addition, they provide guidance in the development of a new process and can reduce both time and capital requirements. The utility of a process model depends strongly on its predictive capabilities. The predictions should be reliable over wide ranges of charge stock compositions and process conditions. Catalytic cracking has been an important petroleum refining process for over 30 yr, and considerable research has been conducted with both pure hydrocarbons and gas oils over many different types of cracking catalysts. The results have provided an understanding of the chemical reactions involved and led to the development of improved cracking catalysts and processes. Previously published models generally utilize this knowledge through empirical correlations relating conversion or product selectivity to charge stock properties and process variables. The identification of lumped species whose reaction rate constants are invariant with feedstock composition and source provides a more fundamental basis for predicting charge stock and process variable effects.

In this work, a wide variety of charge stocks were cracked in a fluidized dense-bed reactor. Detailed analysis of the molecular compositions of the charge stocks and products provided the necessary data to develop a predictive kinetic model. Rate constants and activation energies were calculated for lumped species including paraffins, naphthenes, aromatic rings, and aromatic substituent groups. The reliability of the kinetic predictions for various charge stocks over a wide range of process conditions has been shown.

CONCLUSIONS AND SIGNIFICANCE

The reaction kinetics of catalytic cracking is presented, based on a reaction scheme that includes paraffins, naphthenes, aromatic rings, and aromatic substituent groups in light and heavy fuel oil fractions. The kinetic model also accounts for nitrogen poisoning, aromatic adsorption, and time dependent catalyst decay. The conversion of these lumped species to gasoline, light products, coke, heavy fuel oil, and light fuel oil can be readily calculated by these kinetics. In addition, the detailed composition of the heavy and light fuel oil fractions can be tracked, increasing the utility of the model for predicting recycle behavior and physical properties of the products. The invariant kinetic parameters (rate constants and activation energies) allow the conversion and product selectiv-

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