The Effect of Interfacial Tension Gradients on the Flow Structure of Single Drops or Bubbles Translating in an Electric Field

Stream functions, interfacial velocities, and terminal velocities are computed for spherical drops or bubbles supporting interfacial tension gradients and translating in creeping flow in an electric field imposed in the direction of translation. In particular, the case in which a trace of surfactant is present is considered, and it is found that such material may produce quasi-stagnant zones along the interface either near the poles or the equator. Terminal velocities may be either increased or decreased relative to the value obtained in the absence of the electric field.

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SCOPE

Earlier work has shown the ability of electric fields to generate circulatory flows in drops or bubbles that are either stationary or translating by gravity, and experimental results suggest the importance of such flows in enhancing the rate of mass or heat exchange between a drop and its surroundings. On the other hand, the effect of interfacial tension gradients, particularly as caused by the presence of traces of surfactant, has been thoroughly investigated and shown (in the usual case) to retard significantly interfacial velocity in the rear stagnation region and to reduce terminal velocity. The present work examines theoretically the combined effects of an interfacial tension gradient, drop translation, and an electric field on the flow structure of a drop or bubble and its surroundings. The simultaneous consideration of all three of these effects is necessary to the assessment of the promise of electric fields for enhancing mass or heat exchange rates in, for example, liquid extraction or direct-contact heat transfer operations.

CONCLUSIONS AND SIGNIFICANCE

Expressions are derived for the stream functions, interfacial velocity, and terminal velocity for a drop or bubble under the combined influence of gravitational translation, interfacial tension variation, and an electric field. Numerical results are presented for specific cases in which an interfacial tension gradient derives from the presence and steady state distribution of a trace of surfactant at the interface. Depending on the electrical propreties of the system, the surfactant will tend to concentrate, producing quasi-stagnant zones either at the two poles of the drop or near its equator. The terminal velocity may be either increased or decreased relative to its value in the absence of an electric field. The results for the flow properties of drops or bubbles in the presence of interfacial tension gradients and an electric field may be used to assess the importance of electroconvection in mass or heat exchange processes involving drops or bubbles.

INTRODUCTION

Ample experimental evidence exists to demonstrate that the imposition of an electric field may significantly increase mass (or heat) transfer rates in dropwise liquid extraction or heat exchange (Thornton, 1968; Bailes and Thornton, 1971; Harker and Ahmadzadeh, 1974; Bailes, 1981) and gas absorption by liquid droplets (Carleson and Berg, 1983). One contribution to such enhancement may be drop circulation caused by interaction of the electric field with the electric charge distribution it induces at the droplet interface, as first described by G. I. Taylor (1966) for a stationary drop and pictured in Figure 1(a). Interfacial flow is directed from the poles toward the equator if the product of the dielectric constant and electrical resistivity is greater for the drop than for the surrounding medium, and the reverse if that product is greater for the external phase. Morrison (1977) and Griffiths and Morrison (1979) have computed the resulting creeping flow electroconvective increases in transfer rate and found them to be potentially very significant for the stationary drop case. More recently, Chang et al. (1982) and Chang and Berg (1983) have examined the hybrid flow that occurs when a drop is translating by gravity in an electric field, as pictured in Figure 1(b), and have computed the enhancement in transfer rate over that which would exist in the absence of the electric field. The relative importance of the electrical contribution to convective transport was characterized in terms of a single dimensionless parameter dependent on the electric field strength and both the electrical and hydrodynamic properties of both fluids.

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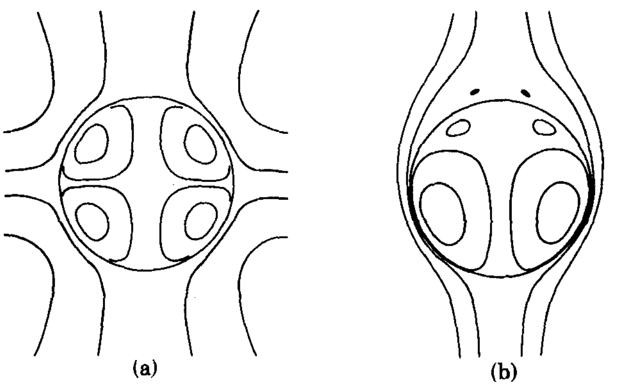

Figure 1. Pattern of streamlines for (a) a drop at rest in a vertically oriented electric field, and (b) a drop falling in a vertically oriented electric field, under conditions such that $W = 2.0$.

While some systems were found to be highly susceptible to electroconvective effects, many others were not. The employment of appropriate extraction solvent systems, or their modification through the addition of traces of appropriate nontransferring solutes (generally to incrrease the electrical conductivity of the less conductive phase), in order to maximize electroconvective enhancement of mass or heat exchange, appears to show significant promise.

Present analyses of drop circulation in the presence of electric fields do not account for the presence of interfacial tension gradients that generally develop around the periphery of the drop during heat or mass transfer. Such gradients may be especially significant if traces of surface active agents are present. It is well known that for this reason creeping flow circulation of a drop or bubble moving through a viscous medium as first described by Hadamard and Rybczynski is seldom realized in practice. Surfactant is swept toward the rear stagnation point of the drop or bubble, establishing a concentration gradient along the drop interface. This produces an interfacial tension gradient with tension highest at the forward stagnation point and lowest at the rear stagnation point, in opposition to the shearing action of the relative motion of the external phase. The interfacial tension could thus reduce or eliminate entirely the internal circulation that would otherwise develop within the drop or bubble, reducing significantly its terminal velocity and rate of heat or mass exchange with surroundings (Kronig and Brink, 1950). Frumkin and Levich, as reviewed in Levich (1962), initially envisioned a continuously varying surfactant concentration about the drop from front to rear, while Savic (1953), based on direct photographs of circulating drops, proposed the formation of a "stagnant cap" of surfactant at the rear of the drop, with the front virtually swept clear of surfactant. The Levich model was developed further by Schechter and Farley (1963), Newman (1967), and Wasserman and Slattery (1969), while the Savic model was refined by Griffiths (1962) and Davis and Acrivos (1966). The problem of the retardation of droplet motion by surfactant has been treated in a more general way by Saville (1973), LeVan and Newman (1976), Harper (1982) and Holbrook and LeVan (1983). The particular role of interfacial viscosity was examined by Agrawal and Wasan (1979) and LeVan (1981) and was found to be important only if rather large values for such viscosities were presumed.

The present work seeks to assess the effect of interfacial tension gradients, particularly as they are developed by the presence of surfactants, in the flow behavior of drops in the presence of electric fields. Any evaluation of electroconvective effects on transport rates would appear to require such consideration because of the potential surface activity of a transferring solute, the virtually universal presence of surfactant contamination, and the probable strong adsorbability of additives that might be used to modify the electrical properties of the system for purposes of promoting electroconvection. Specifically, we seek to determine the interfacial distribution of surfactant under various conditions, the corresponding interfacial velocity distribution, and the terminal velocities. The influence of the changes in flow structure on convective heat or mass transfer will be considered in a later communication.

The following analysis treats a spherical droplet in steady creeping flow through an infinite medium and in the presence of a uniform electric field parallel to the direction of drop translation (i.e., vertical). We assume the electrical Reynolds number (the ratio of the rate of transport of electricity by fluid convection to its rate of transport by conduction) to be sufficiently small that the fluid flow will not affect the spatial distribution of the electric field, and also we assume that any electromagnetic effects due to finite current densities are negligible. The fluids are Newtonian and of constant properties. Any surfactant species present is assumed nonionic, and its presence is assumed to impart no interfacial viscosity to the system or any variation in interfacial electrical conductivity.

ANALYSIS

Stream Functions

We now derive the stream functions for a translating droplet and its surrounding medium subject to the above-stated assumptions when there exists along the droplet interface an arbitary, axisymmetric interfacial tension gradient, which may be the result of mass transfer of a surface active solute to or from the droplet, or may be developed through the action of surfactant additives or contaminants. As in earlier analyses not considering either the presence of surfactant or an electric field, the differential equations for the system are:

$$D^4\Psi_i = 0, \; i = 1,2 \tag{1}$$

where

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

and

$$D^4 = (D^2)^2$$

Subscript 1 denotes the continuous or exterior phase; 2, the drop or interior phase. Stokes stream functions are defined by

$$u_{r_i} = -\frac{1}{r^2\sin\theta}\frac{\partial\Psi_i}{\partial\theta}$$

$$u_{\theta_i} = \frac{1}{r\sin\theta}\frac{\partial\Psi_i}{\partial r} \tag{2}$$

These differential equations must be solved subject to the appropriate boundary conditions. With the applied electrical field parallel to the direction of gravity, axial symmetry is preserved. Thus we have

$$\psi_1 \rightarrow \tfrac{1}{2}Ur^2\sin^2\theta \qquad \text{as } r \rightarrow \infty$$

$$u_{r_2}, u_{\theta_2} \neq \infty \qquad \text{at } r = 0$$

$$\psi_1 = \psi_2 = 0 \qquad \text{at } r = a$$

$$u_{\theta_1} = u_{\theta_2} \qquad \text{at } r = a \tag{3}$$

and

$$\tau_{r\theta_1} - \tau_{r\theta_2} + \tau_{r\theta_E} = \frac{1}{a}\frac{d\sigma}{d\theta} \qquad \text{at } r = a$$

where

$$\tau_{r\theta} = -\mu\left[r\frac{\partial}{\partial r}\left(\frac{u_\theta}{r}\right) + \frac{1}{r}\frac{\partial u_r}{\partial\theta}\right]$$

In the last boundary condition above, $\tau_{r\theta_E}$ is the electrically induced tangential stress at the droplet interface.* Taylor (1966) has

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* The effect of the electrical potential gradient may be treated alternatively as a contribution to the total interfacial tension gradient (see, for example, Levich, 1962, pp. 488ff), although there appears to be no advantage to doing so in the present context. The thermodynamic equivalence of such an approach to that of Taylor (1966), used here, rests on the assumption that the influence of electric charges on the thermodynamic interfacial tension is negligible. Such an assumption has been made here and is consistent with assumptions of earlier investigators (see Discussion following Abbas et al., 1967).

shown that

$$\tau_{r\theta_E} = \frac{9E^2\epsilon_2(1 - \epsilon_1 S_1/\epsilon_2 S_2)}{(2 + S_1/S_2)^2} \sin\theta \cos\theta \equiv Q \sin\theta \cos\theta \quad (4)$$

where E is the uniform electrical field intensity, ϵ is permittivity, S is electrical resistivity, and $d\sigma/d\theta$ is the assumed surface tension gradient.

According to Happel and Brenner (1973), the general solutions to Eq. 1 may be written in spherical coordinates as

$$\psi_1 = \sum_{n=2}^{\infty} (A_n r^n + B_n r^{-n+1} + C_n r^{n+2} + D_n r^{-n+3}) C_n^{-1/2}(\cos\theta) \quad (5)$$

and

$$\psi_2 = \sum_{n=2}^{\infty} (A'_n r^n + B'_n r^{-n+1} + C'_n r^{n+2} + D'_n r^{-n+3}) C_n^{-1/2}(\cos\theta) \quad (6)$$

where $C_n^{-1/2}(\cos\theta)$ is the Gegenbauer function of order n and degree $-\tfrac{1}{2}$, which in turn is closely related to the corresponding Legendre polynomial

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

and

$$C_n^{-1/2}(\cos\theta) = \frac{P_{n-2}(\cos\theta) - P_n(\cos\theta)}{2n - 1}, \quad n \geq 2$$

Applying the first four of Eqs. 3, we get

$$A_2 = 0$$

$$A_n = 0 \qquad \text{for } n \geq 3$$

$$A'_n = -C'_n a^2 = -D'_n a^{3-2n} \qquad \text{for } n \geq 3$$

$$B_2 = -Ua^3 - D_2 a^2$$

$$B_n = -D_n a^2 \qquad \text{for } n \geq 3$$

and

$$C_n = B'_n = D'_n = 0 \qquad \text{for all } n$$

Applying the remaining boundary condition and using the orthogonality property of the Gegenbauer functions, we obtain

$$D_2 = -\frac{Ua(2 + 3X)}{2(1 + X)} + \frac{a}{2\mu_1(1 + X)} \int_0^{\pi} C_2^{-1/2}(\cos\theta) \frac{d\sigma}{d\theta} d\theta \quad (7)$$

$$D_3 = -\frac{Qa^3}{5\mu_1(1 + X)} + \frac{3a^2}{2\mu_1(1 + X)} \int_0^{\pi} C_3^{-1/2}(\cos\theta) \frac{d\sigma}{d\theta} d\theta$$

$$D_n = \frac{n(n - 1)a^{n-1}}{4\mu_1(1 + X)} \int_0^{\pi} C_n^{-1/2}(\cos\theta) \frac{d\sigma}{d\theta} d\theta \qquad \text{for } n \geq 4$$

where X is the viscosity ratio ($X \equiv \mu_2/\mu_1$). Derivation of stream functions is completed as we obtain

$$\psi_1 = Ua^2 \left(\frac{r^2}{2a^2} - \frac{2 + 3X}{4(1 + X)} \frac{r}{a} + \frac{X}{4(1 + X)} \frac{a}{r}\right) \sin^2\theta + Va^2 \left(1 - \frac{a^2}{r^2}\right) \sin^2\theta \cos\theta + \frac{r^2 - a^2}{4\mu_1(1 + X)} \sum_{n=2}^{\infty} n(n - 1) \frac{a^{n-1}}{r^{n-1}} \times C_N^{-1/2}(\cos\theta) \int_0^{\pi} C_n^{-1/2}(\cos\theta) \frac{d\sigma}{d\theta} d\theta \quad (8)$$

$$\psi_2 = \frac{Ua^2}{4(1 + X)} \left(\frac{r^4}{a^4} - \frac{r^2}{a^2}\right) \sin^2\theta + Va^2 \left(\frac{r^5}{a^5} - \frac{3}{a^3}\right) \sin^2\theta \cos\theta + \frac{r^2 - a^2}{4\mu_1(1 + X)} \sum_{n=2}^{\infty} n(n - 1) \frac{r^n}{a^n} C_n^{-1/2} \times (\cos\theta) \int_0^{\pi} C_n^{-1/2}(\cos\theta) \frac{d\sigma}{d\theta} d\theta \quad (9)$$

where

$$V = \frac{9E^2 a\epsilon_2(1 - \epsilon_1 S_1/\epsilon_2 S_2)}{10(2 + S_1/S_2)^2 \mu_1(1 + X)} \quad (10)$$

is a characteristic velocity induced by the electric field. In the absence of both the interfacial tension gradient and the gravity-induced circulation, it represents the maximum interfacial velocity generated by the electrical field. In the presence of an interfacial tension gradient, this parameter can still be determined *a priori*, even though it may not be identifiable as the velocity at any specific point in the system. The terminal velocity U is taken positive for either a rising or falling droplet and, in the presence of an interfacial tension gradient, may not be the same as that predicted by Hadamard and Rybczynski, i.e.:

$$U_o = \frac{2ga^2|\rho_2 - \rho_1|(1 + X)}{3\mu_1(2 + 3X)}$$

When $d\sigma/d\theta = 0$ and $U = U_o$, the above stream functions reduce to those of Chang et al. (1982). The stream functions are made dimensionless using the quantity $Ua^2/4(1 + X)$ as the scale factor. Thus

$$\psi_1^* = \frac{\psi_1}{Ua^2/4(1 + X)} = [(2 + 2X)r^{*2} - (2 + 3X)r^* + Xr^{*-1}] \sin^2\theta + W'(1 - r^{*-2}) \sin^2\theta \cos\theta + \frac{r^{*2} - 1}{U\mu_1} \sum_{n=2}^{\infty} n(n - 1) r^{1-n} C_n^{-1/2} \times (\cos\theta) \int_0^{\pi} C_n^{-1/2}(\cos\theta) \frac{d\sigma}{d\theta} d\theta \quad (11)$$

and

$$\psi_2^* = (r^{*4} - r^{*2}) \sin^2\theta + W'(r^{*5} - r^{*3}) \sin^2\theta \cos\theta + \frac{r^{*2} - 1}{U\mu_1} \sum_{n=2}^{\infty} n(n - 1) r^n C_n^{-1/2} \times (\cos\theta) \int_0^{\pi} C_n^{-1/2}(\cos\theta) \frac{d\sigma}{d\theta} d\theta \quad (12)$$

where

$$W' = \frac{4V(1 + X)}{U} \quad (13)$$

W' is a parameter characterizing the relative importance of electroconvective and gravitational effects; it can also be regarded as a dimensionless electrical field strength or electrical pressure.

Terminal Velocity and Interfacial Velocity

The terminal velocity is determined by equating the buoyant force with the drag force on the droplet. In our case the drag force can be shown to be (Happel and Brenner, 1973)

$$F_d = -4\pi\mu_1 D_2 \quad (14)$$

where D_2 has been shown in Eq. 7 to be dependent on the surface tension gradient. If the interfacial tension gradient is zero, D_2 is invariant with respect to the presence of the electrical stress in the limit of creeping flow, and according to Eq. 14, terminal velocity is not altered by the electrical field through the electrohydrodynamic effect under consideration. However, when interfacial tension is permitted to vary around the drop periphery, D_2 may depend indirectly on electrical stress. The electric field influences the flow structure and in turn, the distribution of surfactant and the value of the interfacial tension gradient, $d\sigma/d\theta$. Terminal velocity is thus a function of the imposed electric field:

$$U = U_o + \frac{1}{\mu_1(2 + 3X)} \int_0^{\pi} C_2^{-1/2}(\cos\theta) \frac{d\sigma}{d\theta} d\theta \quad (15)$$

The terminal velocity of the droplet is thus affected by the electrohydrodynamic stress by influencing the surface tension gradient, even in the limit of creeping flow. The above expressions for drag force and terminal velocity reduce to the limiting cases of Hadamand-Rybczynski or Stokes under appropriate conditions, provided the drop is assumed to remain spherical.

The interfacial velocity is extracted in the usual way using Eqs. 2 and 8 and setting $r = a$.

$$u_i = \frac{U}{2(1+X)} \sin\theta + 2V \sin\theta \cos\theta + \frac{1}{2\mu(1+X)} \sum_{n=2}^{\infty} n(n-1) \times \frac{C_n^{-1/2}(\cos\theta)}{\sin\theta} \int_0^{\pi} C_n^{-1/2}(\cos\theta) \frac{d\sigma}{d\theta} d\theta \quad (16)$$

This expression reduces to the Hadamard-Rybczynski result:

$$u_{i_o} = \frac{U_o}{2(1+X)} \sin\theta \quad (17)$$

in the absence of both the surface tension gradient and the imposed electrical field.

Surfactant Distribution: A Numerical Example

As discussed above, the steady state distribution of a trace of surfactant in the absence of an electric field has been studied extensively and shown to alter dramatically the flow structure of a translating drop or bubble. The concentration of surfactant in the rear stagnation region severely reduces interfacial velocity in that region and significantly alters the terminal velocity. When an electric field is imposed, the more complex flow structures of the type shown in Figure 1 are produced, and one can anticipate that surfactant films, if present, might concentrate themselves either at both the forward *and* rear stagnation regions or along an equatorial stagnation region, depending on the sense of the electrohydrodynamic flow. We seek here to describe such distributions of surfactant and to determine their effect upon interfacial velocities and terminal velocity.

Surfactant distributions along the drop interface, in the most general case, will depend on the rate of convection-diffusion or surfactant to or from the interface from either or both the bulk phases (alternatively, its rate of adsorption or desorption), the rates of interfacial convection and diffusion, and the rate of film collapse at compressional stagnation points on the interface. We consider here the specific example of a bubble rising in a very dilute solution of a nonvolatile surfactant whose interchange with the surface is governed by diffusion in the liquid. Surface diffusion is neglected and surfactant film collapse is assumed not to occur. The convective diffusion for the external phase describing this situation is

$$u \cdot \nabla C = D_1 \nabla^2 C \qquad \text{for phase 1} \quad (18)$$

with boundary conditions

$$\begin{aligned} C &\to C_\infty && \text{as } r \to \infty \\ \frac{\partial C}{\partial \theta} &= 0 && \text{at } \theta = 0^\circ \\ \frac{\partial C}{\partial \theta} &= 0 && \text{at } \theta = 180^\circ \quad (19) \\ D_1 \frac{\partial C}{\partial r} &= \frac{1}{a \sin\theta} \frac{d}{d\theta} (\Gamma u_i \sin\theta) && \text{at } r = a \end{aligned}$$

where C_∞ is the surfactant concentration at infinity, D_1 is the mass diffusivity of the surfactant in the continuous phase, and Γ is the surface concentration of the surfactant. It is related to the surfactant concentration in the liquid sublayer, C_i, and the surface tension derivative with respect to that concentration through the Gibbs adsorption equation

$$\Gamma = -\frac{C_i}{RT} \frac{d\sigma}{dC_i} \quad (20)$$

and the equilibrium adsorption isotherm

$$\Gamma = K C_i \quad (21)$$

which is taken to be linear, since the surfactant concentration is assumed to be very low.

Nondimensionalization of the above equations and substituting $x \equiv \ln r^*$ yield

$$u_r^* \frac{\partial C^*}{\partial x} + u_\theta^* \frac{\partial C^*}{\partial \theta} = \frac{2}{Pe \cdot e^x} \left(\frac{\partial^2 C^*}{\partial x^2} + \frac{\partial^2 C^*}{\partial \theta^2} + \frac{\partial C^*}{\partial x} + \cot\theta \frac{\partial C^*}{\partial \theta} \right) \quad (22)$$

with

$$C^* = 1 \qquad \text{at } x = N \quad (23)$$

$$\frac{\partial C^*}{\partial \theta} = 0 \qquad \text{at } \theta = 0^\circ \quad (24)$$

$$\frac{\partial C^*}{\partial \theta} = 0 \qquad \text{at } \theta = 180^\circ \quad (25)$$

$$\frac{\partial C^*}{\partial x} = \frac{Pe \cdot K^*}{\sin\theta} \frac{d}{d\theta} (C_i^* u_i^* \sin\theta) \qquad \text{at } x = 0 \quad (26)$$

where

$$C^* = C/C_\infty,\ r^* = r/a$$
$$Pe = 2aU_o/D_1,\ K^* = K/2a$$
$$u_i^* = u_i/U_o$$

The first boundary condition is applied far from the interface. The value of N may vary from 1 to 3, depending on the specific problem concerned.

Following LeVan and Newman (1976), we consider the case when the surfactant concentration is sufficiently low that, to a first approximation, the velocity field will be the same as that corresponding to the absence of surfactant. Thus, in accord with Chang et al. (1982), we obtain

$$\begin{aligned} \frac{U_\sigma}{U_o} &= 1 - \kappa_o C_\infty \\ \frac{U_E}{U_o} &= 1 \quad (27) \\ \frac{U_{\sigma E}}{U_E} &= 1 - \kappa C_\infty = \frac{U_{\sigma E}}{U_o} \\ \frac{U_{\sigma E}}{U_\sigma} &= \frac{1 - \kappa C_\infty}{1 - \kappa_o C_\infty} \end{aligned}$$

and

$$\begin{aligned} \frac{u_{i\sigma}}{u_{io}} &= 1 - \beta_o C_\infty \quad (28) \\ \frac{u_{i_E}}{u_{i_o}} &= 1 + W \cos\theta \\ \frac{u_{i_{\sigma E}}}{u_{i_E}} &= 1 - \frac{\beta C_\infty}{1 + W \cos\theta} \\ \frac{u_{i_{\sigma E}}}{u_{i_o}} &= 1 + W \cos\theta - \beta C_\infty \\ \frac{u_{i_{\sigma E}}}{u_{i_\sigma}} &= \frac{1 + W \cos\theta - \beta C_\infty}{1 - \beta_o C_\infty} = \frac{u_{i_{\sigma E}}/u_{i_o}}{(u_{i_{\sigma E}}/u_{i_o})_{W=0}} \end{aligned}$$

where

$$\kappa = \frac{KRT}{2U_o \mu_1} \int_0^{\pi} C_2^{-1/2}(\cos\theta) \frac{dC_i^*}{d\theta} d\theta \quad (29)$$

and

$$\beta(\theta) = \kappa + \frac{KRT}{U_o \mu_1} \sum_{n=2}^{\infty} n(n-1) \frac{C_n^{-1/2}(\cos\theta)}{\sin^2\theta} \times \int_0^{\pi} C_2^{-1/2}(\cos\theta) \frac{dC_i^*}{d\theta} d\theta \quad (30)$$

Note that κ_o and β_o are for the free-rising case, i.e., $W = 0$. The parameter W here is redefined as $4V(1 + X)/U_o$ for easy comparison with previous results. The above terminal and interfacial velocities are defined in Figure 2, where interrelations of these variables are also depicted.

The surfactant concentration gradient at the interface can now be obtained by solving Eqs. 21 and 25 numerically. We consider

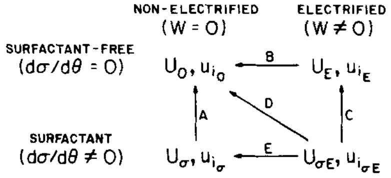

Figure 2. Terminal and interfacial velocity ratios for droplet system under various conditions. Ratio *A* reflects the surfactant effect in a nonelectrified system; *B* the electrohydrodynamic effect in a surfactant-free system; *C*, the surfactant effect in an electrified system; *D*, surfactant and electrohydrodynamic effects; and *E*, the electrohydrodynamic effect in a surfactant-containing system.

a small air bubble rising slowly at 20°C through a continuous phase of a benzene-chlorobenzene solution containing a trace amount of a hypothetical surfactant. The specific values used for properties and parameters are

$a = 1.00 \times 10^{-5}$ m
$\mu_1 = 7.0 \times 10^{-4}$ Pa·s
$\mu_2 = 1.8 \times 10^{-5}$ Pa·s
$\rho_1 = 995$ kg·m^3
$\rho_2 = 1.2$ kg·m^3
$D_1 = 1.53 \times 10^{-10}$ m^2·s^{-1}
$K = 4.00 \times 10^{-7}$ m
$(\epsilon/\epsilon_o)_1 = 4.0$
$(\epsilon/\epsilon_o)_2 = 1.0$
$S_1 = 10^5$ Ω·m
$S_2 = 10^{16}$ Ω·m
$E = 0.03$–0.12 MV·m^{-1}

from which we may compute

$$U_o = 4.58 \times 10^{-4}\ \text{m·s}^{-1}$$
$$Re = 0.013$$
$$Pe = 60$$
$$K^* = 2.00 \times 10^{-2}$$
$$Re_E = 1.6 \times 10^{-4}$$

The electrical Reynolds number, Re_E, is seen to be much less than unity, as has been presumed.

A moderate electrical field intensity, say 0.06 MV·m^{-1}, would yield a W value around unity. With W determined *a priori*, we are able to calculate the electrohydrodynamic effects as a function of W. We resort to an orthogonal collocation on finite elements scheme (employing software ELLPACK 77) to solve the governing elliptic partial differential equation. Typically we used (10×15) elements in the (x,θ) domain. On each element, collocation is based on bicubic Hermite polynomials. The resulting system of linear equations is solved in a band storage mode. In Figure 3 the dimensionless surface concentration of surfactant is plotted against the polar angle measured from the frontal stagnation point. The $W = 0$ curve reproduces the result of LeVan and Newman (1976), who employed a finite-difference scheme. Thus the surfactant is swept to the rear of the droplet, forming a concentration gradient along the bubble interface. When there is an electrical field, but of insufficient strength to cause flow separation ($W < 1$), we see that the surface concentration maximum at the rear is flattened and broadened.

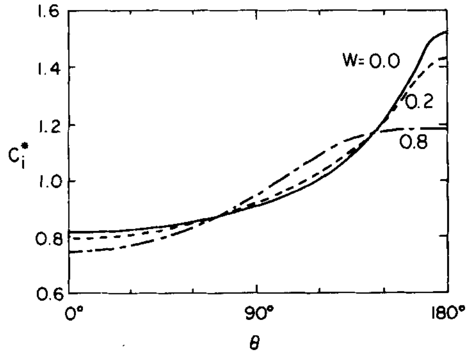

Figure 3. Interfacial surfactant concentration in liquid for electrified bubble system as a function of polar angle measured from the frontal stagnation point. *W* is the dimensionless parameter showing the relative importance of electrical and gravitational effects. *W* = 0 denotes the nonelectrified, free-rising case.

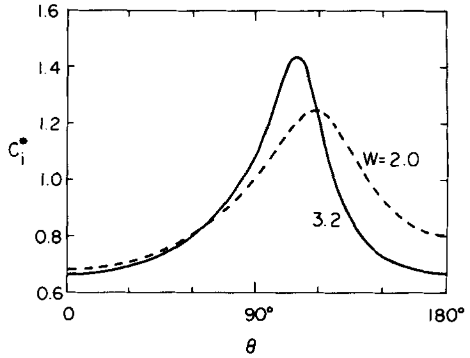

Figure 4. Interfacial surfactant concentration in liquid for electrified bubble system in which electrical field effects are sufficiently great to cause flow separation. Interfacial flow is directed from the poles toward the equator.

When the flow separates at the rear of the bubble, the recirculating flow augmented by the electrohydrodynamic effect tends to push surfactant from the rear of the droplet toward the equator, and the surface concentration of surfactant exhibits the expected maximum along a beltlike region near the line of separation, as shown in Figure 4. For instance, when $W = 2.0$, flow separates near $\cos^{-1}(-\frac{1}{2}) = 120°$, where the surfactant surface concentration reaches a maximum. The resulting surface tension gradient will in turn retard the interfacial velocity primarily near this beltlike region, while the interfacial velocity near the rear stagnation point will not be retarded as much as in the free-rising case. These retardations will lead to a "stagnant belt" between the droplet equator and the rear stagnation point if the rates of surfactant transfer are very low. In Figure 5 we show how the surfactant would be distributed along the interface in several negative W systems, where the electrical tangential stresses tend to induce surface flows from the equator toward the poles. Negative values of W are fictitious in this system, since its electrical properties dictate positive values. When the electrical field is strong enough, two maxima in the surface concentration occur on the droplet interface, a diffuse one at the front and a more sharply delineated one at the rear, resulting in retardations of interfacial velocity mainly in these two regions. In the limit of low rates of surfactant transfer, these would take the form of two "stagnant caps" at the two poles of the droplet.

The surface concentration gradient can be evaluated readily, and several instances are illustrated in Figure 6. We see that the $dC_i^*/d\theta$ (or, in proportion, $d\Gamma/d\theta$) curves change significantly in shape on increasing the electrical field intensity by even a small amount. When separation occurs, $dC_i^*/d\theta$ changes even more

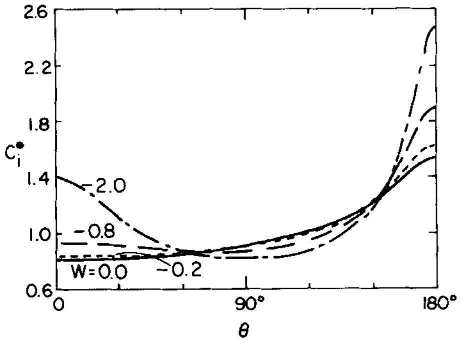

Figure 5. Interfacial surfactant concentration in liquid for electrified bubble system if electrically-induced circulation is from equator toward poles.

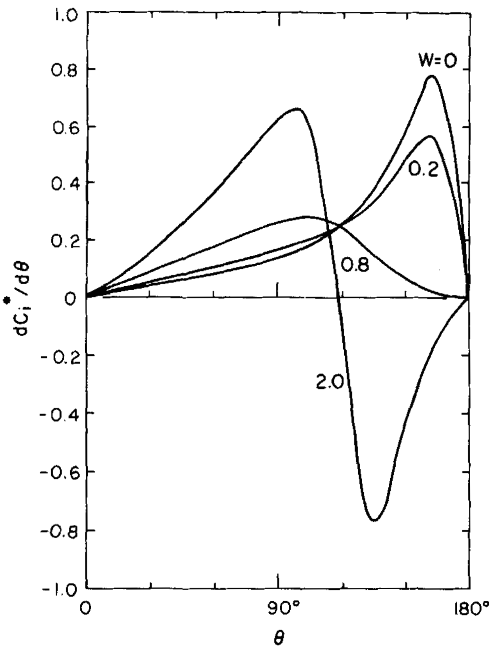

Figure 6. Surface concentration gradient of surfactant for electrified bubble system as a function of polar angle.

dramatically. Knowing $dC_i^*/d\theta$ enables one to evaluate K and $\beta(\theta)$ by using a suitable integration scheme, e.g., the Runge-Kutta method, so that terminal velocity and interfacial velocity can be calculated. For the concentration of surfactant, $C_\infty = 5.0 \times 10^{-5}$ mol·m^{-3} in the liquid phase far from the droplet, Figure 7 shows several β's for different electrical field intensities.

Referring to Eq. 27, the terminal velocity passes through a minimum and then increases as the electrical field strength (and hence W) is increased from zero. Thus, in the presence of surfactant, the electrohydrodynamic effect does influence the terminal velocity. In addition, interfacial velocities may be retarded appreciably. Figure 8 illustrates the ratio of interfacial velocities showing the effect of surfactant at several electrical field intensities. It is seen that the surfactant distribution significantly reduces the surface mobility at the rear portion of the droplet for $W < 1$.

DISCUSSION

The above results correspond to a Peclet number of 60, and the agreement with results of LeVan and Newman (1976) in the absence of an electric field is excellent. Other things being equal, raising the Peclet number (e.g., by having a smaller diffusivity) augments the sweep-over of the surfactant to the stagnation region(s) so that the maxima in C_i^*, $dC_i^*/d\theta$, and $d\sigma/d\theta$ are all sharpened (Chang, 1983). In the limit, stagnant caps or a belt would be observed. The prediction of the resulting cap angles or belt angles *per se* would, however, require the full solution of the flow equations for the case of very low surfactant exchange rates. Realistically, surface diffusion and monolayer collapse would have to be taken into account.

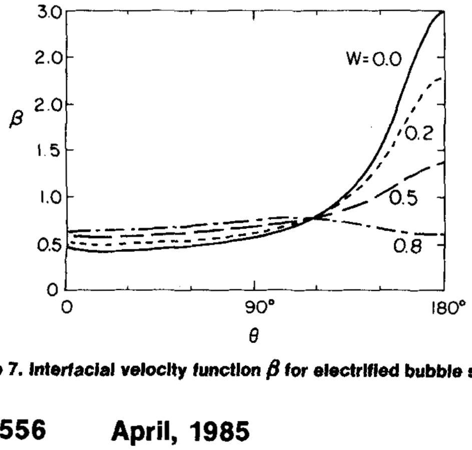

Figure 7. Interfacial velocity function β for electrified bubble system.

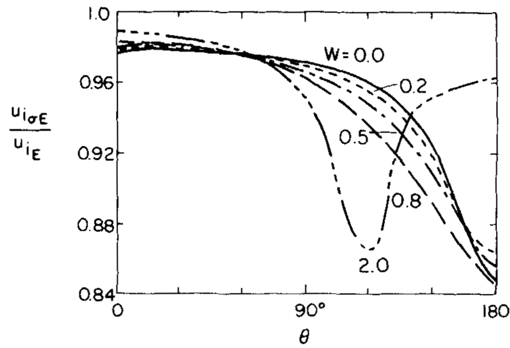

Figure 8. Ratio of interfacial velocities showing the retardation of surfactant at several electrical field intensities. C_∞ = 0.05 mmol·m^{-3}.

While solving the mass transfer equations for the surfactant, we used the velocity components that would obtain in the absence of surfactant so that the solution is strictly valid only at vanishingly low surfactant concentrations, and only small alterations in the qualitative features of the flow field, such as terminal velocity, can be calculated. Solving the coupled momentum and mass balance equations simultaneously would be expected to yield very nearly the same type of surfactant distributions, however, especially when the surfactant concentration is not very high. Our solution to the bubble-liquid case should also be representative of more general fluid systems. Our intention has been to demonstrate the most important flow characteristics in the presence of gravity, the imposed electrical field, and an interfacial tension gradient. These are revealed in Figures 3 through 8.

In particular, we have predicted the existence of quasi-stagnant zones along the interface either near the poles or the equator for realistic values of the fluid properties, electrical properties, and moderate electric field intensities.

ACKNOWLEDGMENT

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NOTATION

A_n,B_n,C_n,D_n = coefficients in Eq. 5
A_n',B_n',C_n',D_n' = coefficients in Eq. 6
a = droplet radius
C = concentration of surfactant
C_i = surfactant concentration in equilibrium with Γ
C_∞ = surfactant concentration far away from droplet
$C_n^{-1/2}(\cos\theta)$ = Gegenbauer function of order n and degree $-1/2$
D = mass diffusivity
E = uniform electrical field intensity
F_d = drag force in Eq. 14
g = acceleration of gravity
K = adsorption coefficient
Pe = Peclet number
$P_n(\cos\theta)$ = Legendre polynominal or degree n
Q = quantity defined in Eq. 4
R = gas constant
r = radial coordinate

Re = $aU\rho/\mu$; Reynolds number
Re_E = $\epsilon SU/a$, electrical Reynolds number
S = resistivity
T = absolute temperature
U = terminal velocity of droplet
$\mathbf{u}$ = velocity vector
u_i = interfacial velocity
u_r = radial velocity
u_θ = tangential velocity
V = electrically generated speed defined by Eq. 10
W = $4V(1 + X)/U_o$
W' = $4V(1 + X)/U$
X = viscosity ratio, μ_2/μ_1
x = $\ln r^*$

Greek Letters

β = interfacial velocity function defined by Eq. 30
Γ = interfacial concentration of surfactant
ϵ = permittivity, ϵ_o = permittivity of free space
θ = polar angle from frontal stagnation point
κ = terminal velocity parameter defined by Eq. 29
μ = viscosity
ρ = density
σ = interfacial or surface tension
$\tau_{r\theta}$ = tangential stress
ψ = Stokes stream function

Subscripts

1 = continuous phase
2 = droplet phase
E = electrified, surfactant-free system
o = nonelectrified, surfactant-free system
σ = surfactant-containing system
σE = electrified, surfactant-containing system

Other

$*$ = nondimensionalized variable

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