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EMULSION STABILITY: AN ANALYSIS OF THE EFFECTS OF BULK AND INTERFACIAL PROPERTIES ON FILM MOBILITY AND DRAINAGE RATE

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Abstract—A hydrodynamic model is developed to predict the kinetics of thinning of emulsion films, such as those existing between two approaching liquid droplets or a drop coalescing at a bulk interface. The present analysis includes the effects of surfactants present in both the film and the drop phases, interfacial tension, interfacial viscosities and their gradients at the liquid–liquid interface on the rate of film drainage. The analysis accounts for the flow in the drop as well as in the film phases. The theoretical predictions are in good agreement with the limited experimental results of Traykov *et al.* (1977).

INTRODUCTION

Coalescence of liquid drops plays an important role in a large number of chemical engineering operations involving liquid–liquid contacting, transportation, and separation processes. The rate of coalescence of drops depends on the rate of drainage of the intervening film. Although there have been some major breakthroughs in recognizing the factors which affect coalescence, the phenomenon is not yet fully understood. One of the main reasons is that coalescence occurs in the interfacial region, which often contains surface-active agents or macromolecules which are known to display a variety of rheological properties. Surfactants, trace impurities and polymeric substances at fluid–fluid interfaces exert a significant influence on the phase separation processes by modifying the interfacial mobility and flow behavior (Berg 1972; Wasan & Mohan 1977).

Coalescence may occur when two drops or bubbles in a fluid dispersion, as in emulsion or foam systems, come very close to each other. In other instances, the drops or bubbles may form a stable aggregate. If the colliding drops have axial symmetry, the process of coalescence can be split into (a) mutual approach of two deformed droplets to form a plane-parallel film and (b) thinning of that film to a critical thickness at which the film becomes unstable, ruptures, and the two drops unify into a single larger droplet. This larger droplet may in turn disappear upon coalescence. The velocity of droplets during stage (a) is relatively high so that their lifetime is essentially determined by stage (b). There are instances when the lifetime of the intervening liquid film also depends on the rate of film collapse (Ivanov 1980).

The earliest models of emulsion stability concerned the coalescence of single droplets with planar liquid–liquid-interfaces (Jeffreys & Hawksley 1965; Woods & Burrill 1972; Liem & Woods 1974). In these early studies, experiments were directed mainly towards measuring the rest time of droplets and hence the effect of surfactant concentration on drop interface coalescence. These studies resulted in the important finding that coalescence is extremely sensitive to surfactant congregation at the interface.

Reynolds (1886) idealized the axi-symmetric drainage of a liquid film between two identical droplets by approximating the deformed area between the droplets by two rigid parallel disks. Results of many investigations dedicated to the study of kinetics of thinning have been interpreted by means of Reynolds' equation (MacKay & Mason 1963). However, due to the

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mobility of the interfaces, the rate of thinning can be several times greater than predicted by Reynolds' equation (Hartland 1967).

The influence of interfacial tension gradients on the tangential movement of the interface itself has been examined by Lee & Hodgson (1968), and the effect of mobility on drop coalescence times in dispersions has been discussed.

The hydrodynamic behavior of systems with liquid–liquid interfaces strongly depends on the liquid flow in the dispersed as well as film phases. Murdoch & Leng (1971) have solved for the flow in the film, but the flow in the drops.is accounted for by introducing some adjustable parameters which need to be determined experimentally. On the basis of the flat disk model, Reed *et al.* (1974a, b) have studied the effect of hydrodynamic coupling of the two phases on the thinning of an unbounded emulsion film from pure liquids. Ivanov & Traykov (1976) have solved the flow equations for both the film and drop phases and have deduced an equation for velocity of thinning of a emulsion film without the presence of a surfactant.

Jones & Wilson (1978) have studied the film drainage problem analytically for the case of a drop of dense liquid sinking through a less dense liquid. They have calculated the circulations induced in the drop and in the lower bulk fluid. They have also examined the effect of the constriction in the film thickness at its periphery and concluded that its presence tends to slow down the drainage.

Although films with pure liquids can be formed and investigated (Lang & Wilke 1971), in practice, emulsion systems contain considerable quantities of surfactant (Becher 1965), so that studies with surfactant stabilized emulsion films are of greatest industrial interest (Sherman 1968).

It is well-known that the presence of surfactants retard drainage of foam and emulsion films. According to Boussinesq (1913) this effect can be accounted for by introducing the concept of surface viscosities—dilational and shear. According to Levich (1962), the dilational surface viscosity is equivalent to the Marangoni–Gibbs' effect: the moving liquid carries surfactant away, thus causing perturbation in the equilibrium surfactant concentration at the interface. This results in interfacial tension gradient and surfactant transport from the bulk liquids to the interface. Traykov & Ivanov (1977) investigated the effect of surfactants on the velocity of thinning of plane-parallel emulsion films using the method suggested by Levich and by assuming surface shear viscosity to be equal to zero. In more recent publications, Ivanov *et al.* (1979, 1980) have pointed out the important role surface viscosity plays in the wave motion for the rupture of emulsion films.

Barber & Hartland (1976) have considered the effect of surface shear and dilational viscosities on the axisymmetric drainage of planar foam films. However, the effect of mass transfer interaction is not included in their analysis.

In a yet unpublished work, Good (1974) analyzed the plane-parallel film model by including the viscosity of the drop phase and continuous phase. He included the effect of interfacial shear and dilational viscosities but assumed that they were a weak function of surfactant concentration.

The above literature survey covers only those models for the film drainage problem which are based on the plane-parallel approach of two droplets. This survey is by no means complete, and the reader is referred to a more recent review article by Ivanov (1980) for further details. Actually, thinning is much more complex than is pictured by the plane-parallel film model. The film is not uniform and rupture occurs at the thinnest point. Dimitrov & Ivanov (1978) have demonstrated that when the interfaces are at a short distance from each other, the film can be considered as being plane-parallel. Scheludko (1967) has pointed out that with capillary radius $<10^{-3}$ m and film thickness $<10^{-7}$ m the film thins without a dimple. Manev *et al.* (1982) reported that the film is plane-parallel for film radius $<10^{-4}$ m. Hence the assumption of a plane-parallel film is justified for small drops.

It remains to be pointed out that instrumentation for the measurement of interfacial rheological properties such as interfacial shear and dilational viscosities have only been refined in recent years (Gardner & Schechter 1976; Wasan & Mohan 1977; Oh & Slattery 1978; Wasan *et al.* 1979; Maru *et al.* 1979; Maru & Wasan 1979) with the result that their role as significant parameters in industrial processes such as foam and emulsion systems is only now being clarified (Slattery 1974, 1979; Wasan *et al.* 1978, 1979, 1980; Flummerfelt 1980; Krieg *et al.* 1981).

The objective of the present work is to develop a hydrodynamic model which is capable of predicting kinetic behavior of surfactant stabilized emulsion films. Specifically, the scope of this study is limited to clearly delineating the influence of both interfacial tension and interfacial viscosities and their gradients on the dynamic behavior of thin liquid films associated with droplet coalescence. The effect of surfactant partitioning on the rate of film thinning has been studied when a surfactant is soluble in (a) the continuous phase only; (b) the dispersed phase only; and (c) in both the continuous and dispersed phases. The present analysis accounts for both flow in the dispersed phase and mass transfer interactions involving surface and bulk diffusion. Surfactant transfer from the dispersion and dispersed phases onto the interface is assumed to be diffusion controlled. Further, we limit our attention to liquid films so thin that Reynolds' lubrication approximation is justified. The plane-parallel film assumption restricts the analysis to films of small radii.

The present analysis uses a plane parallel film (flat disk model) and is based on an assumption that the driving force causing film drainage remains constant throughout the film thinning process. Our work, which is an extension and supplement to that of Good (1974), Ivanov & Traykov (1976) and Traykov & Ivanov (1977), explicitly shows the effects of interfacial viscosities and interfacial tension gradients (or the Marangoni–Gibbs effect) on interfacial mobility and rate of drainage of thin liquid films. A comparison has been made of the present theory to the only available experimental results, those of Traykov *et al.* (1977) on drainage of thin liquid films in oil-in-water and water-in-oil emulsion systems.

FORMULATION OF THE PROBLEM

For simplicity, we consider a symmetrical system made of two identical droplets moving towards each other with the same velocity V along the z-axis. We shall use the flat disc model (Lee & Hodgson 1968; Murdoch & Leng 1971; Ivanov & Dimitrov 1974; Traykov & Ivanov 1977). Figure 1 shows a circular emulsion film surrounded by a biconcaved meniscus. Due to the natural symmetry of the system, we use cylindrical coordinates and all calculations are done only for $z' \geq 0$.†

The following simplifying assumptions were made:

(1) The rheological behaviour of both the bulk liquids and adsorbed layers is Newtonian.

(2) In the absence of surface disturbances the film remains plane-parallel during the process of thinning.

(3) The amplitudes of surface waves are small enough so that a hydrodynamic treatment can be carried out using linearized wave theory. In this case the boundary conditions are to be applied to the undisturbed surface (Levich 1962; Ivanov *et al.* 1970).

(4) Surface disturbances have no effect on the film thinning (Ivanov *et al.* 1970; Ivanov & Dimitrov 1974).

(5) The flow in the film obeys the simplified Navier Stokes equations (valid for $h'/R \ll 1$ and low Reynolds number) known from lubrication theory.

(6) Creeping flow is assumed in the dispersed phase.

(7) The effect of gravity is negligible.

(8) Since drainage is a slow process, a quasi-steady approach is employed.

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†All dimensional quantities are indicated with a prime (′).

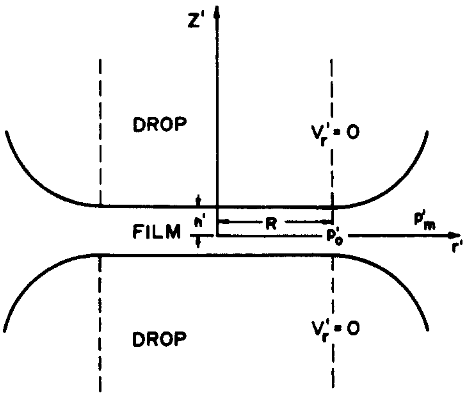

Figure 1. Film configuration and coordinate system.

The dimensionless hydrodynamic equations for the film phase are given by (Levich 1962; Kochin *et al.* 1965)

$$\frac{\partial^2 V_r}{\partial z^2} = \frac{\partial p}{\partial r} \qquad [1]$$

$$\frac{\partial p}{\partial z} = 0 \qquad [2]$$

$$\nabla_r V_r + \frac{\partial V_z}{\partial z} = 0 \qquad [3]$$

where

$$\nabla_r = \frac{1}{r}\frac{\partial}{\partial r} r.$$

Denoting all quantities referring to the dispersed phase by a caret (ˆ), the set of dimensionless hydrodynamic equations is:

$$\frac{1}{a}\frac{\partial \hat{p}}{\partial r} = \nabla^2 \hat{V}_r - \frac{\hat{V}_r}{r^2} \qquad [4]$$

$$\frac{1}{a}\frac{\partial \hat{p}}{\partial z} = \nabla^2 \hat{V}_z \qquad [5]$$

$$\nabla_r \hat{V}_r + \frac{\partial \hat{V}_z}{\partial z} = 0 \qquad [6]$$

where

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}.$$

The dimensionless quantities are defined as

$$V_r = \frac{R}{\nu} V'_r;\; r = \frac{r'}{R};\; p = \frac{\rho R^2}{\mu^2} p';\; a = \frac{\hat{\mu}}{\mu};\; z = \frac{z'}{R}\,.$$

R being the film radius, and ρ, μ, and ν being bulk density, dynamic and kinematic viscosities of the film phase liquid respectively. V_r and V_z denote the velocity components in r- and z-directions, and p denotes pressure.

For small values of Peclet's number ($V'h'/D$), the surfactant distribution in the system is described by

$$\nabla^2 c = 0 \qquad [7]$$

$$\nabla^2 \hat{c} = 0 \qquad [8]$$

where c (dimensionless concentration) $= (c' - c_0')/c_0'$ and c_0' denotes the bulk concentration of the surfactant.

Since the outflow of the liquid from the film initiates the motion of the liquid in both the dispersion phase and the meniscus, a precise hydrodynamic description of the system under consideration is a complex task. Our main objective here is to seek the correlation between the rate of film thinning and the force causing the drainage of the film. Investigations of liquid flow in foam systems have indicated that dissipation of energy decreases sharply with increasing distance between interfaces, so that energy is mainly dissipated in a narrow region proximate to the symmetry axis. Since most of the energy is dissipated in the region $0 < r' < R$, there is no need to consider the liquid motion beyond this region (Ivanov & Traykov 1976). Thus when solving [1]–[8], the following conditions are employed.

$$\left.\begin{array}{l} V_r = \hat{V}_r = U(r) \\ V_z = \hat{V}_z = -V \end{array}\right\} \text{ at } z = h \qquad \begin{array}{r} {[9]} \\ {[10]} \end{array}$$

$$\left.\begin{array}{r} \hat{V}_r = 0 \\ p = p_0 \\ c = 0 \\ \hat{c} = 0 \end{array}\right\} \text{ at } r = 1 \qquad \begin{array}{r} {[11]} \\ {[12]} \\ {[13]} \\ {[14]} \end{array}$$

$$\left.\begin{array}{r} \dfrac{\partial V_r}{\partial z} = 0 \\ \dfrac{\partial c}{\partial z} = 0 \end{array}\right\} \text{ at } z = 0 \qquad \begin{array}{r} {[15]} \\ {[16]} \end{array}$$

$$\left.\begin{array}{r} \hat{V}_r = 0 \\ \hat{V}_z = -V \\ \hat{p} = \hat{p}_0 \\ \hat{c} = 0 \end{array}\right\} \text{ as } z \to \infty \qquad \begin{array}{r} {[17]} \\ {[18]} \\ {[19]} \\ {[20]} \end{array}$$

where $V' = -\mathrm{d}h'/\mathrm{d}t'$ is the rate of thinning of the film, $U(r)$ is the radial velocity of the interface, $\hat{p}_0$ is the pressure in the dispersed phase far away from the interface, and p_0 is the pressure in the hypothetical equilibrium film of the same thickness. This pressure is related to the pressure p_m in the meniscus through the equation

$$p_0 = p_m + \Pi \qquad [21]$$

where Π is the disjoining pressure (see e.g. Scheludko 1966; Toshev & Ivanov 1975).

All functions giving the solution of [1]–[8] must be finite at $r = 0$.

Conditions [9] and [10] result from the very formulation of the problem. Equations [12] and [13] follow from the assumption that the liquid in the meniscus is immobile, and [17]–[19] account for the vanishing of the radial motion of the liquid in the dispersed phase as $z \to \infty$. Equation [11] is equivalent to the condition $\hat{\psi}(1, z) = \text{Constant}$, where $\hat{\psi}(r, z)$ is the stream function in the dispersed phase. In other words, the cylinder $r = 1$ $(z \geq h)$ is a stream surface with dispersed phase liquid circulating in it during the film thinning process. Although, the boundary condition of zero radial velocity at $r = 1$ in the dispersed phase is rather arbitrary, it is convenient to use it in the absence of the complete solution of the transport equations in the continuous as well as in the dispersed phases.

The solution of the system [1]–[8] must also satisfy the surfactant conservation law and tangential stress balance on the interface. In order to write these boundary conditions, additional simplifying assumptions are made (Levich 1962; Radoev *et al.* 1974; Ivanov & Dimitrov 1974; Traykov & Ivanov 1977):

(9) Surfactant transfer is initiated only by the liquid flow; i.e. with no liquid flow there is an equilibrium distribution of the surfactant in the system.

(10) Surfactant transfer from the dispersion and dispersed phases onto the interface is diffusion controlled.

(11) For the thinning film, the local values of interfacial and bulk surfactant concentrations Γ' and c' deviate slightly from their equilibrium values Γ'_0 and c'_0; i.e.

$$|\Gamma' - \Gamma'_0| \ll \Gamma'_0; \quad |c' - c'_0| \ll c'_0.$$

Hence the local values of interfacial tension σ and surface concentration Γ' are expanded in terms of $c' - c'_0$ or $\hat{c}' - \hat{c}'_0$ and only linear terms in this series are considered.

The dimensional forms of the surfactant conservation law and tangential stress boundary condition at the surface $z' = h'$ are

$$\frac{1}{r'}\frac{\partial}{\partial r'}(r' U' \Gamma') - \frac{D'_s}{r'}\frac{\partial}{\partial r'}\left(r' \frac{\partial \Gamma'}{\partial r'}\right) = -D \frac{\partial c'}{\partial z'} + \hat{D}\frac{\partial \hat{c}'}{\partial z'} \qquad (22)$$

$$\mu \frac{\partial V'_r}{\partial z'} - \hat{\mu}\frac{\partial \hat{V}'_r}{\partial z'} = \frac{\partial}{\partial r}[\mu'_s \nabla_r U'] - 2\frac{\partial \epsilon'}{\partial r'}\frac{U'}{r'} + \frac{\partial \sigma}{\partial r'} \qquad (23)$$

where μ'_s denotes the sum of interfacial shear, ϵ', and dilational, κ', viscosities, which shall be called interfacial viscosity for the sake of brevity. D and D'_s are the bulk and surface diffusion coefficients, respectively. σ is interfacial tension.

The surfactant balance [22] was phenomenologically formulated by Levich (1962) and has been recently derived by Brenner & Leal (1978) on the basis of statistical mechanical principles. The last term $(\partial\sigma/\partial r')$ in [23] accounts for the Marangoni–Gibbs effect.

When the surfactant is soluble in both the dispersion and dispersed phases, its concentrations c' and $\hat{c}'$ at the surface $z' = h'$ in dimensional form are related through

$$\Gamma'(c') = \Gamma'(\hat{c}') \qquad [24]$$

Using assumptions (10) and (11) one obtains

$$\left(\frac{\partial\Gamma}{\partial c}\right)^{0'}(c'-c_0') = \left(\frac{\partial\Gamma}{\partial\hat{c}}\right)^{0'}(\hat{c}'-\hat{c}_0') \text{ at } z'=h' \qquad [25]$$

where the symbol $(\ )^0$ represents the equilibrium value of the interfacial property measured at the bulk concentration of surfactant.

The assumption of local equilibrium with respect to the distribution of the surfactant between the two phases allows one to write

$$\frac{\partial\Gamma'}{\partial r'} = \left(\frac{\partial\Gamma}{\partial c}\right)^{0'}\frac{\partial c'}{\partial r'}\bigg|_{z'=h'} = \left(\frac{\partial\Gamma}{\partial\hat{c}}\right)^{0'}\frac{\partial\hat{c}'}{\partial r'}\bigg|_{z'=h'} \qquad [26]$$

$$\frac{\partial\sigma}{\partial r'} = \left(\frac{\partial\sigma}{\partial c}\right)^{0'}\frac{\partial c'}{\partial r'}\bigg|_{z'=h'} = \left(\frac{\partial\sigma}{\partial\hat{c}}\right)^{0'}\frac{\partial\hat{c}'}{\partial r'}\bigg|_{z'=h'} \qquad [27]$$

etc.

The dimensionless forms of the surfactant conservation law and tangential stress boundary conditions become

$$\Gamma_0\nabla_r U = -\frac{1}{Sc}\frac{\partial c}{\partial z} + \frac{1}{S\hat{c}}\frac{a}{\gamma}\frac{\partial\hat{c}}{\partial z}$$

$$+\begin{cases} \dfrac{D_s}{r}\left(\dfrac{\partial\Gamma}{\partial c}\right)\dfrac{\partial}{\partial r}\left(r\dfrac{\partial c}{\partial r}\right) & \text{(a)} \\ & \text{at } z=h \\ \dfrac{D_s}{r}\left(\dfrac{\partial\Gamma}{\partial\hat{c}}\right)\dfrac{\partial}{\partial r}\left(r\dfrac{\partial\hat{c}}{\partial r}\right) & \text{(b)} \end{cases} \qquad [28]$$

$$\frac{\partial V_r}{\partial z} - a\frac{\partial\hat{V}_r}{\partial z} = \mu_s\frac{\partial}{\partial r}(\nabla_r U)$$

$$+\begin{cases} \left[\dfrac{\partial\mu_s}{\partial c}\nabla_r U - 2\left(\dfrac{\partial\epsilon}{\partial c}\right)\dfrac{U}{r}\right]\dfrac{\partial c}{\partial r} + \dfrac{1}{We}\left(\dfrac{\partial\sigma}{\partial c}\right)\dfrac{\partial c}{\partial r} & \text{(a)} \\ & \text{at } z=h \\ \left[\dfrac{\partial\mu_s}{\partial\hat{c}}\nabla_r U - 2\left(\dfrac{\partial\epsilon}{\partial\hat{c}}\right)\dfrac{U}{r}\right]\dfrac{\partial\hat{c}}{\partial r} + \dfrac{1}{We}\left(\dfrac{\partial\sigma}{\partial\hat{c}}\right)\dfrac{\partial\hat{c}}{\partial r} & \text{(b)} \end{cases} \qquad [29]$$

We introduce the following symbols for convenience:

$$K_\sigma = -\left(\frac{\partial\sigma}{\partial c}\right)^{0'}; \quad K_\epsilon = \left(\frac{\partial\epsilon}{\partial c}\right)^{0'}; \quad K_\kappa = \left(\frac{\partial\kappa}{\partial c}\right)^{0'}.$$

The dimensionless quantities are defined as

$$\left(\frac{\partial\sigma}{\partial c}\right) = \left(\frac{\partial\sigma}{\partial c}\right)^{0'}\frac{c_0'}{\sigma}; \quad \frac{\partial\epsilon}{\partial c} = \left(\frac{\partial\epsilon}{\partial c}\right)^{0'}\cdot\frac{c_0'}{\mu R}; \quad \left(\frac{\partial\mu_s}{\partial c}\right) = \left(\frac{\partial\mu_s}{\partial c}\right)^{0'}\cdot\frac{c_0'}{\mu R}$$

$$\left(\frac{\partial\Gamma}{\partial c}\right) = \left(\frac{\partial\Gamma}{\partial c}\right)^{0'}\frac{1}{R}; \quad Sc = \frac{\mu}{\rho D}; \quad We = \frac{\mu^2}{R\rho\sigma}; \quad D_s = \frac{D_s'\rho}{\mu};$$

$$\Gamma_0 = \frac{\Gamma_0'}{c_0 R}; \quad \mu_s = \frac{(\kappa+\epsilon)'}{\mu R}; \quad \gamma = \frac{\hat{\rho}}{\rho}.$$

SOLUTION OF THE PROBLEM

Flow in the film phase

Since our method of solution of the hydrodynamic equations for the film phase with corresponding boundary conditions is the same as that presented in detail by Radoev *et al.* (1974), we here only adduce the final results.

$$V_r = U(r)\left[1+\frac{3}{2}\frac{z^2-h^2}{h^2}\right]-\frac{3}{4}\frac{rV}{h^3}(z^2-h^2) \qquad [30]$$

$$V_z = \frac{3V}{2h^3}\left[\frac{z^3}{3}-h^2 z\right]-\frac{1}{r}\frac{\partial}{\partial r}(rU)\left[z+\frac{3}{2h^2}\left(\frac{z^3}{3}-h^2 z\right)\right] \qquad [31]$$

$$p = p_0+\frac{3V}{4h^3}(1-r^2)-\frac{3}{h^2}\int_r^1 U(r)\,\mathrm{d}r. \qquad [32]$$

In the above equations the radial interfacial velocity, U, and the film thinning velocity, V, are coupled with the solution of the problem in the drop phase. This is presented as follows:

Flow in the drop phase

Using [4]–[6], a more convenient relation for the flow in the drop phase is derived.

$$\left[\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{\partial^2}{\partial z^2}-\frac{1}{r^2}\right]^2 \hat{V}_r = 0. \qquad [33]$$

We seek a solution of the form

$$\hat{V}_r = \hat{V}_r^{(1)}+z\hat{V}_r^{(2)}. \qquad [34]$$

where $\hat{V}_r^{(1)}$ and $\hat{V}_r^{(2)}$ are solutions of the equation

$$\frac{\partial^2 \hat{V}_r}{\partial r^2}+\frac{1}{r}\frac{\partial \hat{V}_r}{\partial r}+\frac{\partial^2 \hat{V}_r}{\partial z^2}-\frac{\hat{V}_r}{r^2}=0. \qquad [35]$$

Using [34] and [35] the solution of [33] is given by

$$\hat{V}_r = \sum_{n=1}^{N}[A_n+B_n z]\,\mathrm{e}^{-\lambda_n z}J_1(\lambda_n r). \qquad [36]$$

where λ_n being nth root of $J_1(\lambda)=0$.

Continuity equation [6] along with [36] and corresponding boundary conditions lead to

$$\hat{V}_z = (h-z)\sum_{n=1}^{N} A_n\frac{\lambda_n}{1+\lambda_n h}\mathrm{e}^{-\lambda_n z}J_0(\lambda_n r)-V \qquad [37]$$

$$B_n = -\frac{\lambda_n}{1+\lambda_n h}A_n \qquad [38]$$

$$U(r) = \sum_{n=1}^{N} A_n\frac{\mathrm{e}^{-\lambda_n h}}{1+\lambda_n h}J_1(\lambda_n r). \qquad [39]$$

It can be seen from [39] that the radial velocity of the interface at the film periphery is zero.

This is a direct manifestation of [11]. For the case of negligible viscous effects in the dispersed phase, Barber & Hartland (1976) have advanced semi-quantitative ideas on the sensitivity of several boundary conditions at $r = 1$.

(a) *Surfactant soluble in both the film and drop phases.* The surfactant repartition influences the radial interfacial and thinning velocities through [28] and [29]. The solution of [7] and [8] with corresponding boundary conditions gives the concentration profiles in the film and drop phases.

$$c = \sum_{n=1}^{N} c_n \cosh(\alpha_n z) J_0(\alpha_n r) \qquad [40]$$

$$\hat{c} = \sum_{n=1}^{N} \hat{c}_n \, e^{-\alpha_n z} J_0(\alpha_n r) \qquad [41]$$

where α_n being nth root of $J_0(\alpha) = 0$.

From [25], [28], [40] and [41] we have

$$\sum_{k=1}^{N} A_k P_k(h) J_0(\lambda_k r) = -\sum_{n=1}^{N} c_n Q_n(h) J_0(\alpha_n r) \qquad [42]$$

where

$$P_k(h) = \Gamma_0 \frac{\lambda_k}{1+\lambda_k h} e^{-\lambda_k h},$$

and

$$Q_n(h) = D_s \left(\frac{\partial \Gamma}{\partial c}\right) \alpha_n^2 \cosh(\alpha_n h) + \left[\frac{1}{Sc} \sinh(\alpha_n h) + \frac{1}{S\hat{c}} \frac{a}{\gamma} \frac{\left(\frac{\partial \Gamma}{\partial c}\right)}{\left(\frac{\partial \Gamma}{\partial \hat{c}}\right)} \cosh(\alpha_n h)\, \alpha_n \right]$$

γ being the ratio of drop and film phase densities.

We expand $J_0(\lambda_k r)$ in terms of $J_0(\alpha_n r)$, i.e.

$$J_0(\lambda_k r) = \sum_{n=1}^{N} M_k^n J_0(\alpha_n r). \qquad [43]$$

Using the orthogonality property of Bessel's functions it can be shown that

$$M_k^n = \frac{2\alpha_n}{\alpha_n^2 - \lambda_k^2} \frac{J_0(\lambda_k)}{J_1(\alpha_n)}. \qquad [44]$$

Combining [42] and [43] one obtains

$$c_n = -\frac{1}{Q_n(h)} \sum_{k=1}^{N} M_k^n P_k(h) A_k. \qquad [45]$$

In the lubrication approximation, the force balance in dimensionless form is (Ivanov & Dimitrov 1974; Dimitrov & Ivanov 1978)

$$F = 2\pi \int_0^1 (p - p_m) r \, dr. \qquad [46]$$

Substitution of the pressure profile from [32] results in

$$F=\frac{3\pi}{h^2}\sum_{n=1}^{N}A_n\frac{e^{-\lambda_n h}}{\lambda_n(1+\lambda_n h)}J_0(\lambda_n)+\frac{3\pi}{8h^3}V \qquad [47]$$

where

$$F=\pi R^2\Delta p$$

Δp being the pressure difference causing drainage and is the sum of attractive and disjoining pressures. The velocity of thinning, V, is given by

$$V=\frac{8h^3}{3\pi}F-8h\sum_{n=1}^{N}A_n\frac{e^{-\lambda_n h}}{1+\lambda_n h}J_0(\lambda_n). \qquad [48]$$

Substitution of [31], [37], [39] and [40] into [29] provides a relation between the A_k's and the system parameters at a given h.

$$\sum_{k=1}^{N}[a_k^{(1)}(r,h)+a_k^{(2)}(r,h)+a_k^{(3)}(r,h)-a_k^{(4)}(r,h)-a_k^{(5)}(r,h)]A_k=R^{(1)} \qquad [49]$$

where

$$a_k^{(1)}(r,h)=\frac{3}{h}\frac{e^{-\lambda_k h}}{1+\lambda_k h}J_1(\lambda_k r)+\frac{12r}{h}\frac{e^{-\lambda_k h}}{\lambda_k(1+\lambda_k h)}J_0(\lambda_k)$$

$$a_k^{(2)}(r,h)=2a\lambda_k\frac{e^{-\lambda_k h}}{1+\lambda_k h}J_1(\lambda_k r)$$

$$a_k^{(3)}(r,h)=\mu_s\lambda_k^2\frac{e^{-\lambda_k h}}{1+\lambda_k h}J_1(\lambda_k r)$$

$$a_k^{(4)}(r,h)=\frac{\Gamma_0}{We}\frac{\partial\sigma}{\partial c}\sum_{n=1}^{N}\frac{1}{Q_n(h)}\frac{2\alpha_n^2}{(\alpha_n^2-\lambda_k^2)}\frac{J_0(\lambda_k)}{J_1(\alpha_n)}\cdot$$

$$\frac{\lambda_k}{1+\lambda_k h}e^{-\lambda_k h}\cosh(\alpha_n h)J_1(\alpha_n r)$$

$$a_k^{(5)}(r,h)=\left[\frac{\partial\mu_s}{\partial c}P^N-2\frac{\partial\epsilon}{\partial c}\frac{1}{r}\sum_{n=1}^{N}A_n\frac{e^{-\lambda_n h}}{1+\lambda_n h}J_1(\lambda_n r)\right]\cdot Q_k^N$$

$$P^N=\sum_{n=1}^{N}A_n\frac{\lambda_n}{1+\lambda_n h}e^{-\lambda_n h}J_0(\lambda_n r)$$

$$Q_k^N=\Gamma_0\sum_{n=1}^{N}\frac{1}{Q_n(h)}\frac{2\alpha_n^2}{(\alpha_n^2-\lambda_k^2)}\frac{J_0(\lambda_k)}{J_1(\alpha_n)}\frac{\lambda_k}{1+\lambda_k h}e^{-\lambda_k h}\cosh(\alpha_n h)J_1(\alpha_n r)$$

$$R^{(1)}=\frac{4hFr}{\pi}.$$

(b) *Surfactant soluble in film phase.* In this case there is no surfactant diffusion from the dispersed phase onto the interface and the solution is given by (49) with

$$Q_n(h) = D_s\left(\frac{\partial\Gamma}{\partial c}\right)\alpha_n^2\cosh(\alpha_n h) + \frac{1}{Sc}\,\alpha_n\sinh(\alpha_n h).$$

(c) *Surfactant soluble in drop phase.* In this case the surfactant conservation law and tangential stress boundary conditions are given by [28b] and [29b] respectively. Since there is no surfactant diffusion from the film phase onto the interface, the term, $(1/Sc)(\partial c/\partial z)$, in [28b] does not contribute to the surfactant flux.

Combining [28b], [39] and [40] it can be shown that

$$\sum_{k=1}^{N} A_k P_k(h) J_0(\lambda_k r) = -\sum_{n=1}^{N} \hat{c}_n Q_n(h) J_0(\alpha_n r)$$

$$Q_n(h) = D_s\left(\frac{\partial\Gamma}{\partial\hat{c}}\right)\alpha_n^2\,e^{-\alpha_n h} + \frac{1}{S\hat{c}}\,\alpha_n\,e^{-\alpha_n h}. \qquad [50]$$

$P_k(h)$ is the same as given earlier.

The solution in this case is still given by [49] with

$$a_k^{(4)}(r,h) = \frac{\Gamma_0}{We}\frac{\partial\sigma}{\partial\hat{c}}\sum_{n=1}^{N}\frac{1}{Q_n(h)}\frac{2\alpha_n^2}{(\alpha_n^2-\lambda_k^2)}\frac{J_0(\lambda_k)}{J_1(\alpha_n)}\frac{\lambda_k}{1+\lambda_k h}\,e^{-\lambda_k h}\,e^{-\alpha_n h}J_1(\alpha_n r)$$

$$Q_k^N(r,h) = \Gamma_0\sum_{n=1}^{N}\frac{2}{Q_n(h)}\frac{\alpha_n^2}{(\alpha_n^2-\lambda_k^2)}\frac{J_0(\lambda_k)}{J_1(\alpha_n)}\frac{\lambda_k}{1+\lambda_k h}\,e^{-\lambda_k h}\,e^{-\alpha_n h}J_1(\alpha_n r)$$

other terms remaining as in the case (a).

METHOD OF SOLUTION

The presence of a non-linearity with respect to the A_k's precludes a direct determination of the A_k's. Hence, an iterative solution of [49] was sought.

At a given film thickness, h, [49] is solved for the A_k's using the collocation method (Finlayson 1972). This technique requires that the equation be satisfied at N collocation points, r_i, $i = 1, 2, \ldots, N$. This, together with the truncation of the series in [49] to N terms, yields sufficient though non-linear equations to evaluate the A_k's.

The system of N non-linear algebraic equations, [49] is quadratic in the unknown A_k's. The system was solved iteratively using direct substitution of various terms. The quadratic terms were written in terms of old and new values of A_k, thus transforming the set of non-linear equations into linear equations. The resultant equations were solved by matrix inversion. Initially the non-linear terms were set equal to zero. The criterion for convergence was chosen to be

$$\sum_{k=1}^{N}\left(\frac{A_{k,\mathrm{old}}}{A_{k,\mathrm{new}}}-1\right)^2 \le 10^{-4}.$$

Once the A_k's have been determined, the velocity of thinning V, is calculated from (48). The drainage time was calculated by numerically integrating the equation

$$t' = -\int_{h'_i}^{h'_f}\frac{dh'}{V'} \qquad [51]$$

where h'_i and h'_f are the initial and final film thicknesses, t', h' and V' in [51] being dimensional quantities.

RESULTS AND DISCUSSION

The simplest model for predicting the rate of film thinning is given by Reynolds (1886). This model does not include the effect of surfactant transfer on the film thinning rate. However, for a constant driving force, F, it gives the slowest film thinning velocity (dimensionless)

$$V = \frac{8h^3}{3\pi}F. \qquad [52]$$

The time (dimensionless $t = (\nu/R^2)t'$) required for the film to drain from an initial thickness, h_i, to final thickness, h_f, is given by

$$t = \frac{3\pi}{16F}\left(\frac{1}{h_f^2} - \frac{1}{h_i^2}\right). \qquad [53]$$

According to [53] an infinite time is required for the film to reach zero thickness. But in practice, at values of film thickness between 300–600°A, a sudden rupture of the film occurs, and the two drops coalesce. In other instances the film stops draining at a particular thickness (of the order of 400°A), and such films are termed stable. The essential conditions for the applicability of the Reynolds' equation [52] are: (1) the interface is considered to be non-deformable; and (2) the interface is tangentially immobile (i.e. $V'_r = 0$). Neither of these two assumptions are strictly true for fluid/fluid interfaces. An interface is likely to be fully mobile only if the liquid is completely free of surface-active agents, whereas an interface saturated with surfactant is not completely immobile and moves tangentially at a rate determined by its interfacial viscosity and the flow fields adjacent to it.

Dimitrov & Ivanov (1978) have shown that if an effective radius $R' = (F'R_c/2\pi\sigma_0)^{1/2}$ is introduced, the functionality of the velocity of thinning of a deformable film with tangentially immobile interface is the same as in [52] except that the numerical coefficient is 2 instead of 8/3. However, in many cases of foam films the effect of interfacial mobility on the approach velocity is the same for both deformable and non-deformable interfaces (Ivanov 1980). Hence the ratio of thinning velocity to Reynolds' velocity represents interfacial mobility which has little or no dependence on the shape of the film.

For the present model the interfacial mobility of emulsion films in the presence of surfactants is given by [48] and [52]

$$\frac{V}{V_{RE}} = 1 - \frac{3\pi}{h^2F}\sum_{n=1}^{N}\frac{e^{-\lambda_n h}J_0(\lambda_n)}{\lambda_n(1+\lambda_n h)}A_n. \qquad [54]$$

Parametric study

Under the assumption of constant driving force throughout the film drainage, we can calculate the unknown A_k's in [49] and the drainage time if the bulk and interfacial properties are known. The values for most of these properties can vary several orders of magnitude from one system to another, depending on the surfactant characteristics. Typical values for the system parameters were chosen as shown in table 1.

The sufficient number of collocation points were arrived at by plotting the drainage time vs interfacial viscosity for different number of collocation points. It was found that $N = 6$ gave sufficiently accurate results. This procedure was also employed even when non-linear terms were present. The solution was checked for multiplicity by using different initial guesses. Whenever the solution converged, it converged to the same single value.

Table 1. System parameters and parametric study of film mobility and drainage phenomena

Parameter	μ Pa.s	$\hat{\mu}$ Pa.s	D m^2/s	$\hat{D}$ m^2/s	D'_s m^2/s	K_σ $\mu N.m^2/mol$	Γ'_o mol/m^2	F' N	h'_i m	h'_f m	$\left(\frac{\partial\Gamma}{\partial c}\right)^{o'}$ m	$\left(\frac{\partial\Gamma}{\partial \hat{c}}\right)^{o'}$ m	R m
Magnitude	10^{-3}	$2x10^{-2}$	10^{-9}	10^{-9}	10^{-9}	$1.6x10^{6}$	$6.5x10^{-9}$	10^{-5}	10^{-7}	$2.5x10^{-8}$	10^{-6}	$5x10^{-7}$	10^{-4}

Figure 2 shows the variation of interfacial mobility as a function of film thickness for different values of interfacial viscosity, μ_s, and interfacial tension gradients with respect to concentration, $K_\sigma(-\partial\sigma/\partial c)$. The effect of K_σ on film drainage time is depicted in figure 3. At high values of $K_\sigma(\geq 10^8)$, bulk and interfacial diffusion can not counter-balance the interfacial tension gradients (the Marangoni–Gibbs' effect) and hence velocity of thinning is essentially given by Reynolds equation [52]. However, for smaller values of K_σ, even at a moderate interfacial viscosity of 10^{-5} Pa.m.s. (10^{-2} surface poise), the thinning or approach velocity is several times greater than Reynolds' velocity. An increase in interfacial viscosity results in decreased interfacial mobility and hence higher drainage time. For low values of interfacial

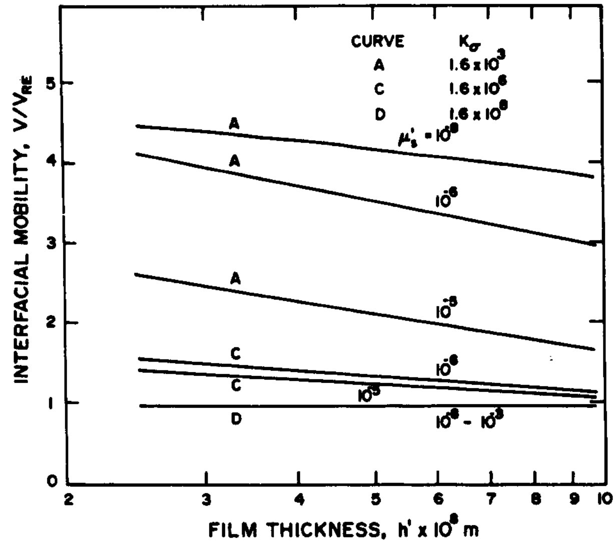

Figure 2. Effect of film thickness on interfacial mobility for various values of μ'_s and K_σ.

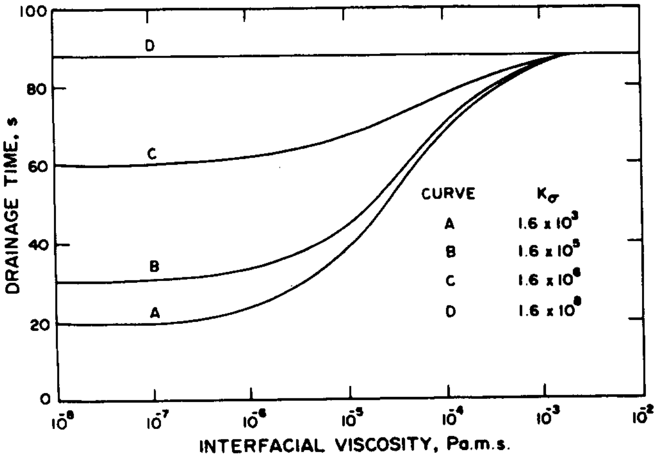

Figure 3. Effect of interfacial viscosity on drainage time for various values of K_σ.

viscosities ($\leq 10^{-6}$ Pa.m.s.), the term containing μ_s in [29] becomes insignificant and hence does not appreciably affect the thinning velocity. At high values of μ'_s ($\geq 10^{-2}$ Pa.m.s.), the interface is rendered immobile and hence the interfacial mobility and drainage time are independent of interfacial viscosity and interfacial tension gradient with respect to concentration.

Figure 4 demonstrates the variation of interfacial mobility with both film thickness and interfacial viscosity as the film radius, R, varies from 5×10^{-5} to 2×10^{-4} m. Figure 5 shows the variation of drainage time with interfacial viscosity at different values of the film radius. As the film radius, R, increases, the contribution of the term containing μ_s in [29] decreases and hence there is an increase in interfacial mobility. However, there is a substantial increase in the drainage time because the Reynolds' velocity decreases sharply with increasing film radius.

At small concentrations of water soluble surfactants, the continuous phase (film phase) viscosity is essentially that of water ($\sim 10^{-3}$ Pa.s). Throughout this parametric study, this value has been used. Figure 6 demonstrates the variation in interfacial mobility due to an increase in

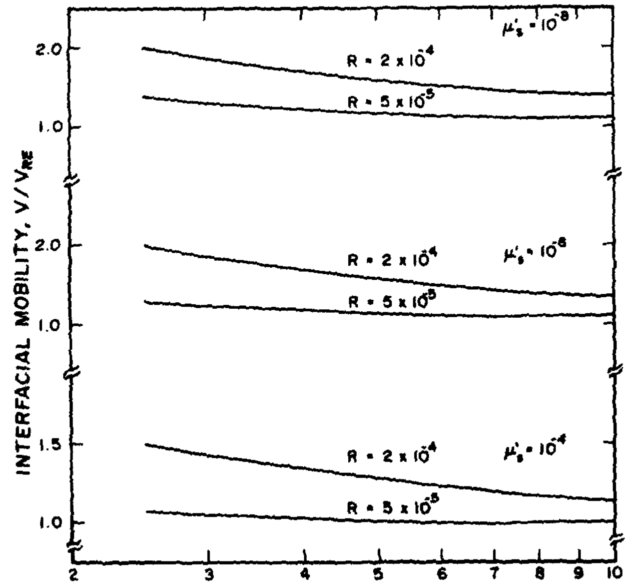

Figure 4. Effect of film thickness on interfacial mobility for various values of μ'_s and R.

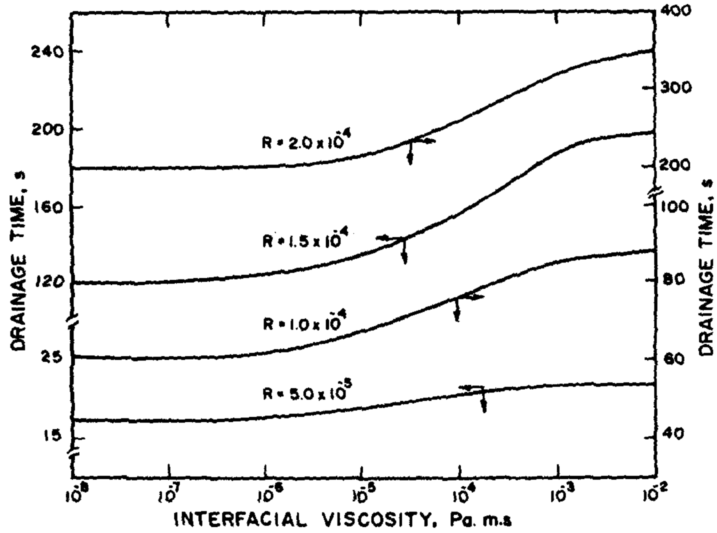

Figure 5. Effect of interfacial viscosity on drainage time for various values of film radius, R.

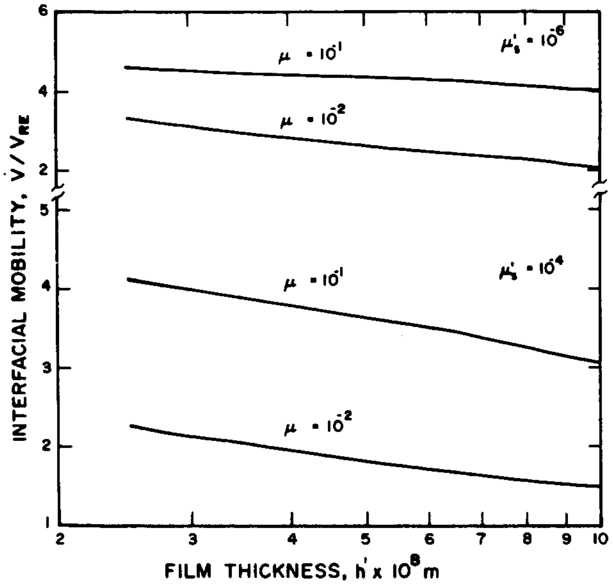

Figure 6. Effect of film thickness on interfacial mobility for various values of μ'_S and μ.

film phase viscosity. An increase in film phase viscosity implies greater resistance to the drainage of the film ($V'_{RE}\alpha 1/\mu$) and hence a significant increase in the drainage time, as shown in figure 7.

The effect of the bulk viscosity of the drop phase on drainage time is shown in figure 8. As is evident from this figure, the drop phase viscosity has no effect on drainage time at high values of the interfacial tension gradient with respect to concentration, K_σ, where the interface is already immobile. Therefore, emulsions behave like foams at high values of K_σ. However, at lower values of K_σ, an increase in the drop phase viscosity lowers the interfacial mobility and hence increases the drainage time, due to the increased bulk stress from the drop phase which opposes the outward flow of film liquid.

During the process of film thinning, the surfactant is swept outwards from the center of the flattened area, thus perturbing the equilibrium surfactant concentration on the interface. The change in surfactant concentration results in surfactant transfer (interfacial and bulk diffusion), which tends to restore the equilibrium distribution of the surfactant on the interface. Interfacial diffusion eliminates interfacial tension gradients, so that an increase in interfacial diffusivity

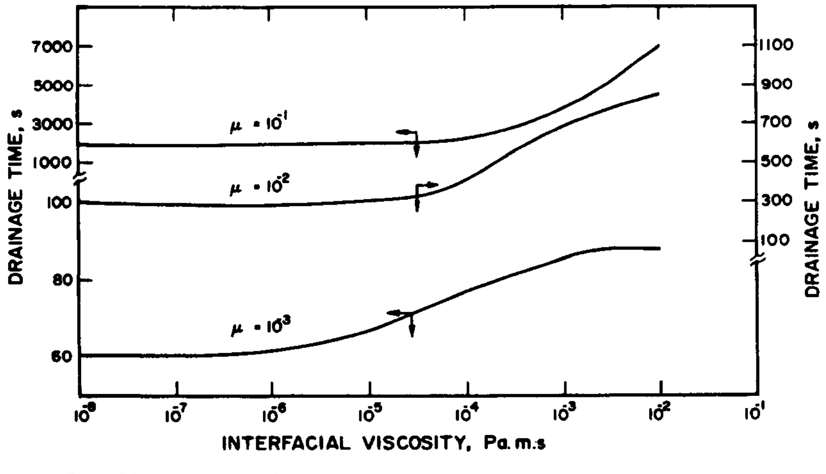

Figure 7. Effect of interfacial viscosity on drainage time for various values of continuous phase viscosity, μ.

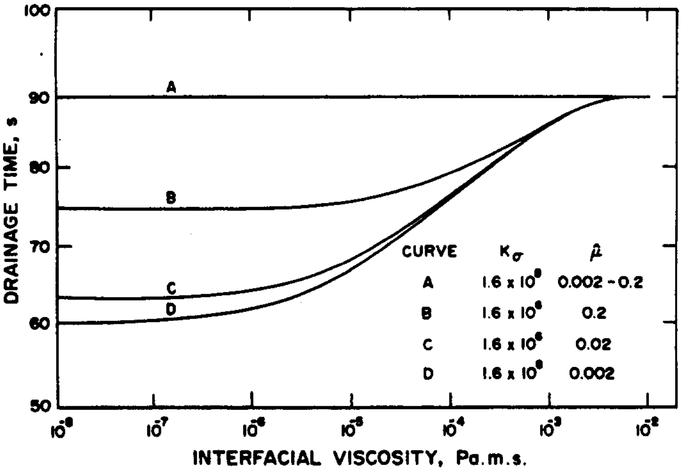

Figure 8. Effect of interfacial viscosity on drainage time for various values of $\hat{\mu}$ and K_σ.

results in increased interfacial mobility and hence faster drainage rate (figure 9). However, for extremely high or low values of K_σ, the drainage time has no dependence on interfacial diffusivity; when K_σ is very large, the Marangoni-Gibbs effect renders the interface immobile, and when K_σ is very small, the velocity of approach is determined by interfacial viscosity.

Film phase diffusivity was found to have very little or no effect on velocity of thinning. However, drop phase diffusivity was found to have a significant effect on interfacial mobility and hence on drainage time. Bulk diffusion from the drop phase was found to be more efficient in promoting interfacial mobility than was bulk diffusion from the film phase and interfacial diffusion. Figure 10 depicts the effect of the drop phase diffusivity on drainage time as a function of interfacial viscosity for two different values of K_σ, the interfacial tension gradient with respect to concentration.

The force causing drainage is the sum of attractive and disjoining forces. A lowering in the interfacial tension decreases capillary suction and hence lowers the thinning velocity. As expected, an increase in driving force, F, causes a lowering of the drainage time as shown in figure 11. However, as it can be readily seen from [48] and [54], the driving force, F, has no effect on the interfacial mobility. In the present study, it has been assumed that this driving force remains constant throughout the film thinning process. However, any force given as a continuous or discrete function of film thickness can be used, with little modification to the present method of solution.

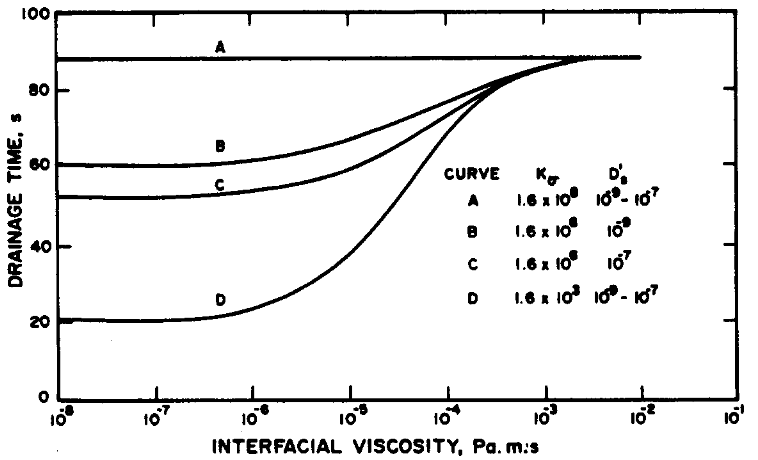

Figure 9. Effect of interfacial viscosity on drainage time for different values of D'_s and K_σ.

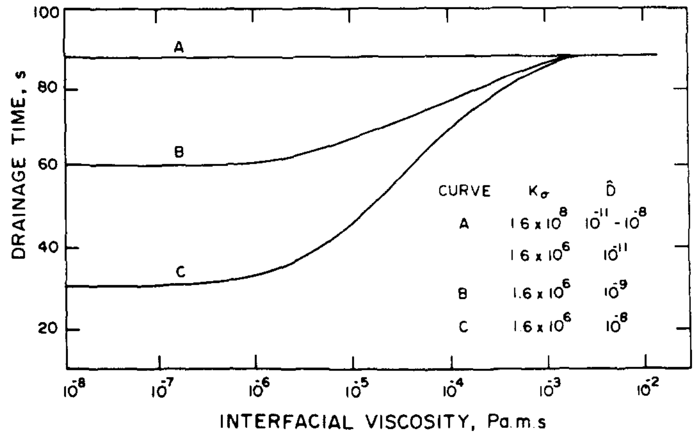

Figure 10. Effect of interfacial viscosity on drainage time for different values of $\hat{D}$ and K_σ.

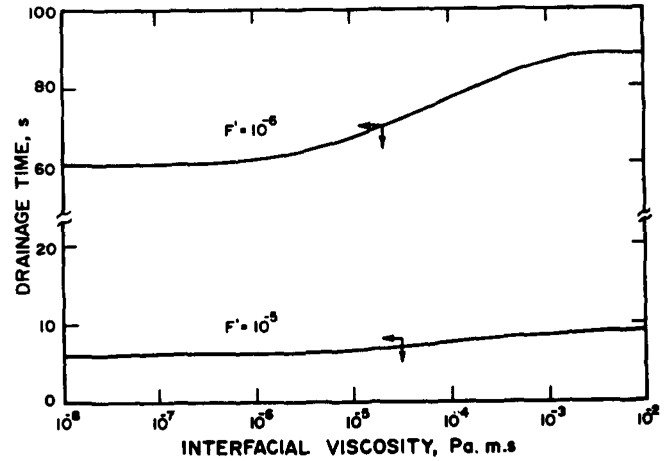

Figure 11. Effect of interfacial viscosity on drainage time for different values of driving force, F'.

The effects of gradients of interfacial shear and dilational viscosities were studied for the following cases: (i) $K_\epsilon = 0$ with K_κ varied from -10^7 to 10^7; (ii) $K_\kappa = 0$ with K_ϵ varied from -10^6 to 10^6; (iii) K_κ and K_ϵ both varied with $|K_\kappa| > |K_\epsilon|$. K_κ and K_ϵ were chosen to be in the range -10^7–10^7 and -10^6–10^6, respectively.

In all the three cases interfacial viscosity gradients had very little or no effect on drainage time.

Figures 12–14 compare the effect of selective surfactant solubility on interfacial mobility (figures 12 and 13) and drainage time (figure 14) for the cases where (a) surfactant is soluble only in the film phase, and (b) surfactant is soluble only in the drop phase. It is noted that lower interfacial mobility and higher drainage times are obtained in the first case, while higher interfacial mobility and lower drainage times are obtained in the second. As pointed out by Lee & Hodgson (1968) and Ivanov (1980), when the surfactant is soluble in the film phase it has to diffuse a long way through the film perimeter. Since the driving force is the gradient of the surfactant concentration along the interface, the diffusion can not eliminate interfacial tension gradient which opposes thinning. When the surfactant is soluble in the drop phase, the surfactant flux is generated by the normal gradient of the concentration and counterbalances the perturbation in interfacial concentration, Γ', caused by the convective flux, resulting in a higher velocity of thinning. The emulsions with surfactant soluble in film phase are thus more stable than those with surfactant soluble in drop phase. This conclusion is in agreement with

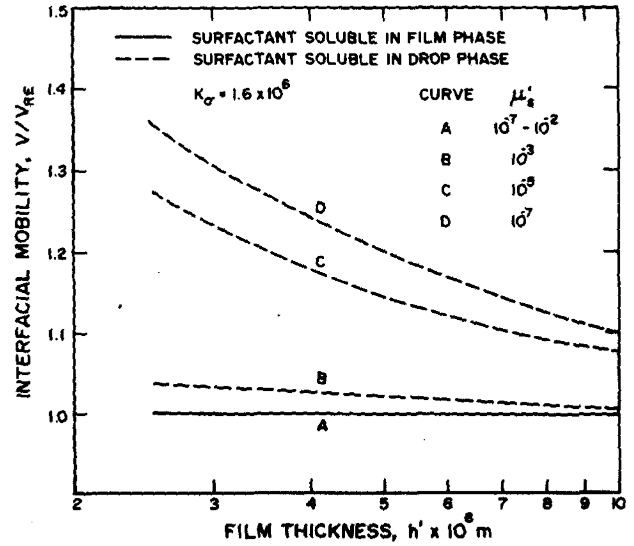

Figure 12. Effect of selective surfactant solubility on interfacial mobility for $K_\sigma = 1.6 \times 10^6$ and for different values of μ'_s.

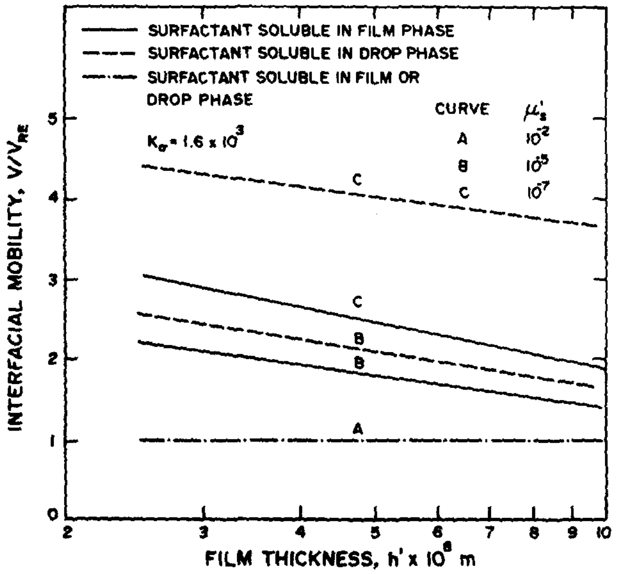

Figure 13. Effect of selective surfactant solubility on interfacial mobility for $K_\sigma = 1.6 \times 10^3$ and for different values of μ'_s.

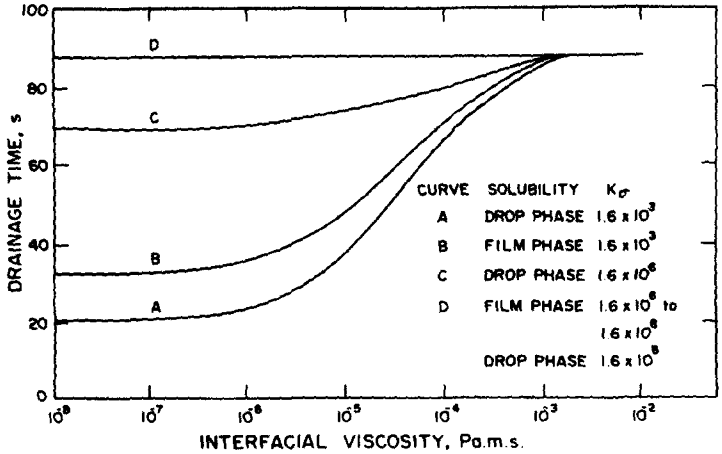

Figure 14. Effect of selective surfactant solubility on drainage time for different values of μ'_s and K_σ.

Bancroft's rule and has been discussed previously by Davies (1957), Sherman (1968) and more recently by Traykov & Ivanov (1977).

It should be pointed out that the rate of coalescence does not depend only on the film thinning velocity but also on the surface hydrodynamic instability or wave behavior. This topic has been of considerable interest in recent years, and the reader is referred elsewhere (Vrij 1966; Vrij *et al.* 1970; Ivanov *et al.* 1970; Patzer & Homsy 1975; Jain & Ruckenstein 1976).

Comparison of theoretical predictions with experimental results

There have been very few experimental investigations concerning drainage of emulsion films. Traykov *et al.* (1977) have investigated the effect of different concentrations of surfactant in the dispersed phase on (a) the velocity of thinning of thin films containing very low concentrations of surfactant soluble in the dispersion medium, and (b) the life time of films of pure liquids. They conducted experiments using the dynamic method attributed to Scheludko and his collaborators (Scheludko & Exerova 1959; Scheludko 1966, 1967). All the investigated films had a radius, $R = 10^{-4}$ m.

We have employed the only available data of Traykov *et al.* (1977) on film thinning to verify some of the predictions of our theoretical model. Since the physical data required for making theoretical predictions were not available for the systems studied by Traykov *et al.* (1977), we have chosen the best known values for some of the properties, and estimated others (see table 2). We have used interfacial tension data reported by the authors to estimate K_σ, Γ_0' and $(\partial\Gamma/\partial c)^{0'}$ values. K_σ value was estimated by assuming the σ_0 vs c_0 curve to be linear. Γ_0' and $(\partial\Gamma/\partial c)^{0'}$ values were estimated using Gibbs adsorption isotherm. Since no interfacial viscosity data were reported by these authors, we assumed the value to be zero for all the systems. This assumption is justified only at low surfactant concentrations. Bulk and interfacial diffusion coefficients were assumed to be 10^{-9} m^2/s for all the systems. Since initial thickness (at $t' = 0$) has not been reported by the authors, the comparison was done with an initial thickness, $h_i' = 10^{-7}$ m to a final thickness, h_f'. All parameters used for the theoretical predictions have been tabulated in table 2. The pressure difference causing drainage, ΔP, was calculated using the following:

$$\Delta p' = \frac{2\sigma_0}{R_c} + \frac{K}{(2h')^3} \qquad [55]$$

where R_c is the capillary radius and K is Hamaker's constant.

Figures 15–17 and table 3 detail the comparison of Reynolds' model and our model against the experimental data. At high surfactant concentrations where the interface is immobile,

Table 2. Parameters used in theoretical predictions for comparison with data of Traykov, *et al.* (1977)

System	Emulsion type	c^w kmol/m^3	c^o kmol/m^3	$\sigma_0 \times 10^3$ N/m	$\mu \times 10^3$ Pa.S	$\beta \times 10^3$ Pa.S	K_σ μNm^2/kmol	Γ_0' kmol/m^2	$(\frac{\partial\Gamma}{\partial c})^{o'}$ m	$h_f' \times 10^{10}$ m	$R_c \times 10^3$ m	$K \times 10^{21}$ N.m Visser (1972)
1	W/O	0	5×10^{-7}	35	0.65	1.0	7.0×10^4	1.4×10^{-14}	2.8×10^{-8}	370	1.45	6
2	W/O	0	1×10^{-1}	28	0.65	1.0	7.0×10^4	2.8×10^{-9}	2.8×10^{-8}	425	1.45	6
3	O/W	1×10^{-7}	0	35	1.0	0.65	5.0×10^5	2.0×10^{-14}	2.0×10^{-7}	385	1.35	4
4 A	O/W	2×10^{-3}	0	34	1.0	0.65	5.0×10^5	4.0×10^{-10}	2.0×10^{-7}	425	1.35	4
4 B	O/W	2×10^{-3}	0	34	1.0	0.65	2.5×10^5	2.0×10^{-10}	1.0×10^{-7}	425	1.35	4

c^w – concentration of sodium octylsulfonate in aqueous phase; c^o – concentration of lauryl alcohol in benzene phase.

Systems:

1. Film, benzene + 5×10^{-7} kmol/m^3 lauryl alcohol; Dispersed phase, water +0.3 kmol/m^3 sodium chloride.
2. Film, benzene +0.1 kmol/m^3 lauryl alcohol; Dispersed phase, water +0.3 kmol/m^3 sodium chloride.
3. Film, water +10^{-7} kmol/m^3 sodium octylsulfonate + 0.3 kmol/m^3 sodium chloride; Dispersed phase, benzene.
4. Film, water +2×10^{-3} kmol/m^3 sodium octylsulfonate + 0.3 kmol/m^3 sodium chloride; Dispersed phase, benzene.

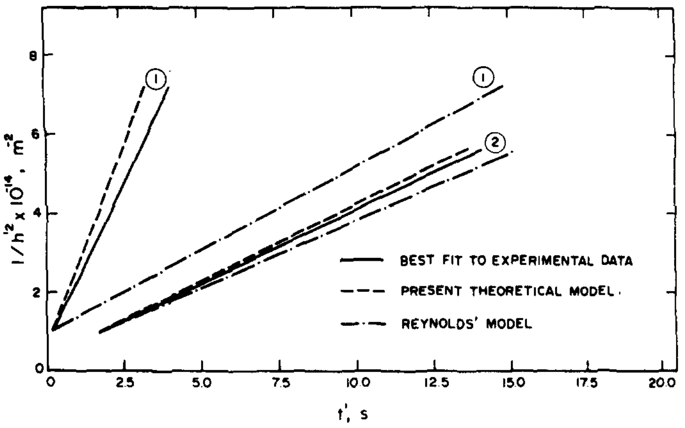

Figure 15. Comparison of theoretical predictions with experimental data for benzene films.

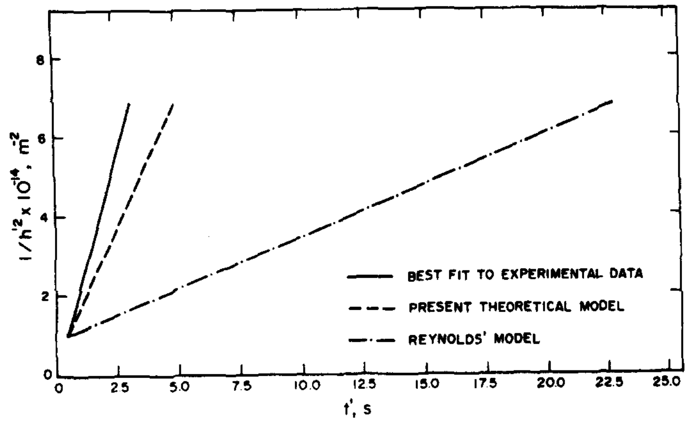

Fig. 16. Comparison of theoretical prediction with experimental data for aqueous film containing 10^{-7} kmol/m^3 sodium octylsulfonate + 0.3 kmol/m^3 sodium chloride.

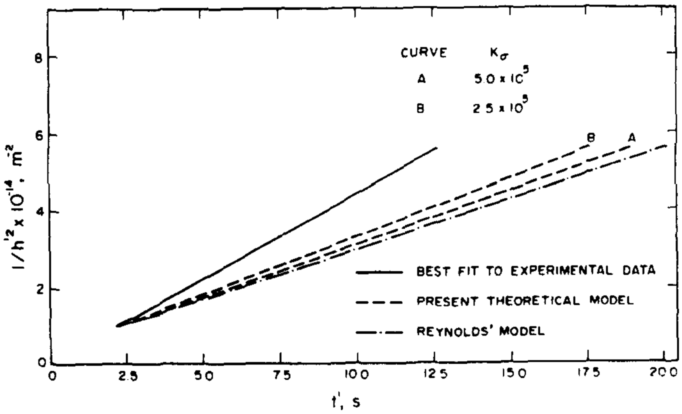

Figure 17. Comparison of theoretical predictions with experimental data for aqueous film containing 2×10^{-3} kmol/m^3 sodium octylsulfonate + 0.3 kmol/m^3 sodium chloride.

Reynolds' model predicts results which are close to the experimental data. However, for low surfactant concentrations, Reynolds' model predicts an extremely slow drainage rate as compared with experimental data. Our present model predicts results which are in fair agreement with experimental data for all the systems studied. It is interesting to note that the proposed model is in better agreement for systems 1 and 2 as compared with systems 3 and 4. Any variations in σ_0 (i.e. $\Delta\sigma_0$) attributed to experimental error will significantly affect the value

Table 3. Comparison of theoretical and experimental drainage times

System	Emulsion Type	c^w kmol/m^3	c^o kmol/m^3	Drainage Time, s		
				Reynolds' model	Present model	Experimental
1	W/O	0	5×10^{-7}	14.8	3.3	4.1
2	W/O	0	1×10^{-1}	15.3	13.6	14.1
3	O/W	1×10^{-7}	0	22.8	4.9	2.9
4 A	O/W	2×10^{-3}	0	20.2	19.0	12.7
4 B	O/W	2×10^{-3}	0	20.2	17.7	12.7

c^w - concentration of sodium octylsulfonate in aqueous phase, c^o - concentration of lauryl alcohol in benzene phase.

Systems:

1. Film, benzene + 5×10^{-7}kmol/m^3 lauryl alcohol; Dispersed phase, water +0.3kmol/m^3 sodium chloride.
2. Film, benzene +0.1 kmol/m^3 lauryl alcohol; Dispersed phase, water+0.3 kmol/m^3 sodium chloride.
3. Film, water +10^{-7}kmol/m^3 sodium octylsulfonate + 0.3 kmol/m^3 sodium chloride; Dispersed phase, benzene.
4. Film, water + 2 x 10^{-3}kmol/m^{3}sodium octylsulfonate + 0.3 kmol/m^3 sodium chloride; Dispersed phase, benzene.

of K_σ for those systems where the variation is large with respect to $\Delta\sigma_0$. For example, for systems 1 and 2 where $\Delta\sigma_0$ is 7×10^{-3} N/m, a 0.25×10^{-3}N/m variation in the reported values for σ_0 will lead to a 7% variation in K_σ. However, for systems 3 and 4 where $\Delta\sigma_0$ is 1×10^{-3} N/m, the same variation in the reported values for σ_0 leads to a 50% variation in K_σ. For systems 3 and 4, K_σ was decreased by a factor of 2 and the model was tested again. For a low surfactant concentration, the change in the value of K_σ did not affect the drainage rate, but for a high surfactant concentration, the change in K_σ resulted in improved agreement with experimental data (System 4B).

A comparison was also made using the model of Traykov & Ivanov (1977). At higher surfactant concentration their model predicts drainage rate similar to Reynolds' model. However, at lower surfactant concentration their model predicts drainage time <0.1 s (Malhotra).

CONCLUSIONS

A theoretical model has been developed to predict the kinetic behavior of surfactant stabilized emulsion films which includes the effects on the rate of film drainage of both interfacial tension and interfacial viscosities and their gradients at the liquid–liquid interface. The analysis takes into account the flow in the drop as well as in the film phases, and also mass transfer interactions.

We have conducted a parametric study involving several interfacial and bulk fluid properties, the combination of which determine the interfacial mobility and drainage time.

The effect of interfacial tension gradient and interfacial shear and dilational viscosities and their gradients on drainage time depend strongly on the partitioning of surfactants. Emulsion systems with surfactants soluble in the film phase thin much more slowly than those with surfactants soluble in the dispersed phase. For diffusion-controlled surfactant transfer, an increase in the total interfacial viscosity results in a decrease in interfacial mobility and thus higher drainage time. This effect is most pronounced at lower values of film thickness, of the order of 10^{-7} m or less.

The presence of an interfacial tension gradient renders the interface immobile, and its effect on interfacial mobility is much more pronounced than that of the total interfacial viscosity. Film thinning, and thereby drainage rate, is significantly affected by the interfacial tension gradient (the Marangoni-Gibbs' effect). This is especially true for systems exhibiting low interfacial viscosities ($\leq10^{-5}$ Pa.m.s.), which may explain why stable emulsions or foams can exist where interfacial viscosity has been observed to be low.

Interfacial mobility and rate of film drainage depend on interfacial viscosity between 10^{-6} and 10^{-3} Pa.m.s. Outside this range, interfacial viscosity has no effect. The following variables decrease interfacial mobility and drainage rate for all values of interfacial viscosity between 10^{-6} and 10^{-3} Pa.m.s.: (i) high value of interfacial tension gradient with respect to concentration; (ii) high drop phase viscosity; (iii) low drop phase diffusivity; (iv) low interfacial diffusivity; and (v) surfactant solubility in continuous (film phase only).

A comparison has been made of the present theory to the limited available data of Traykov *et al.* (1977) on drainage of thin liquid films in water-in-oil and oil-in-water emulsion systems. It is concluded that present model is a significant improvement over Reynolds' model, particularly at low surfactant concentrations where the film mobility is most important. However, a number of interfacial and bulk properties need to be accurately determined through separate experiments in order to further verify our analysis. Further, the velocity of thinning, the critical film thickness, and the radius of the film need to be measured for a number of different surfactant systems in order to make a precise quantitative verification of the theory. Such a study is being undertaken using an incident light interference microscopic technique in our laboratory (Wasan 1981).

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NOTATION

a	ratio of the drop to film phase bulk viscosities
c	surfactant concentration
c_0'	Equilibrium bulk surfactant concentration, kmol/m^3
c^0	concentration of lauryl alcohol in benzene phase, kmol/m^3
c^w	concentration of sodium octylsulfonate in aqueous phase, kmol/m^3
D	bulk diffusivity of surfactant, m^2/s
D_s	interfacial diffusivity of surfactant
F	force causing drainage
h	0.5 film thickness
J_0	Bessel function of zero order
J_1	Bessel function of first order
K	Hamaker's constant, N.m
K_ϵ	$\left(\frac{\partial\epsilon}{\partial c}\right)^{0'}$, μ Pa.m^4.s/kmol
K_κ	$\left(\frac{\partial\kappa}{\partial c}\right)^{0'}$, μPa.m^4.s/kmol
K_σ	$-\left(\frac{\partial\sigma}{\partial c}\right)^{0'}$, μN.m^2/kmol
p	pressure
$\Delta p'$	pressure difference causing drainage, Pa
p_m	pressure in the meniscus
R	radius of the flattened portion of the film, m
R_c	radius of capillary of drop, m
r	radial direction in cylindrical system
Sc	Schmidt number
t	drop coalescence time
U	tangential velocity of the interface
V	velocity of thinning

V_{RE}	Reynolds' approach velocity
V_r	velocity component in direction
V_z	velocity component in z-direction
We	Weber number
z	Axial direction in cylindrical coordinate system

Greek symbols

α_n	nth root of $J_0(\alpha) = 0$
λ_n	nth root of $J_1(\lambda) = 0$
Γ	interfacial excess concentration of surfactant
γ	ratio of drop to film phase densities
ϵ	interfacial shear viscosity
κ	interfacial dilational viscosity
μ	bulk viscosity, Pa.s
μ_s	total interfacial viscosity
Π	disjoining pressure
π	3.1415
ρ	bulk density, Kg/m^3
σ	interfacial tension, N/m
ν	kinematic viscosity, m^2/s
$\hat{\psi}$	stream function in the drop phase

Subscripts and Superscripts

f	final value
i	initial value
0	equilibrium value
$\hat{}$	refers to drop phase
$'$	dimensional variables

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