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On the Viscosity of Dilute Emulsions

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The slow motion of a liquid droplet in a shear flow in the presence of surfactants is studied. The effects of the interfacial viscosity, Gibbs elasticity, surface diffusion and bulk diffusion of surfactants in both phases are taken into account. The analytical solution of the problem for small Reynolds and Peclet numbers gives a simple criterion for estimation of the tangential mobility of the droplet interface. By applying the standard procedure for averaging of the stress tensor flux at an arbitrary surface of the dilute emulsion, an analytical formula for the viscosity of emulsions in the presence of surfactants is derived. The result is a natural generalization of the well-known formula of Einstein for the viscosity of monodisperse dilute suspensions and of the expressions derived by Taylor and Oldroyd for the viscosity of monodisperse dilute emulsions taking into account the Marangoni effect. © 2001 Academic Press

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1. INTRODUCTION

One of the basic problems of physicochemical hydrodynamics is the theoretical interpretation of experimental results for the viscosity of suspensions, emulsions, and foams. In 1906, Einstein (1, 2) showed that a dilute suspension of spherical particles can be considered a continuous phase whose viscosity η_{sus} depends on the particle volume fraction Φ:

$$\frac{\eta_{sus}}{\eta} = 1 + 2.5\Phi + O(\Phi^2). \qquad [1]$$

Here η is the viscosity of the continuos liquid phase. Later Taylor (3) generalized Eq. [1] for emulsion systems taking into account the viscous dissipation of energy due to the flow inside the droplets. The formula of Taylor for the viscosity of emulsion, η_{em}, is similar to Eq. [1],

$$\frac{\eta_{em}}{\eta} = 1 + \frac{\eta + 2.5\eta_d}{\eta + \eta_d}\Phi + O(\Phi^2), \qquad [2]$$

where η_d is the viscosity of the disperse phase (the liquid inside the drops).

Boussinesq (4) postulated the existence of a surface viscosity, conceived as a two-dimensional equivalent of the conventional three-dimensional viscosity possessed by bulk phases. For many years, Boussinesq's solution was accepted as the basis for explaining the anomalous droplet settling velocity measured in the experiments by Lebedev (5) and Silvey (6). The latter authors found that small fluid droplets settle as solid spheres and therefore contradict the theory of Rybczynski (7) and Hadamar (8). Oldroyd (9) combined the theory of Taylor and the idea of Boussinesq and derived a formula for the viscosity of a diluted monodisperse emulsion whose droplets have viscous interfaces:

$$\frac{\eta_{em}}{\eta} = 1 + \frac{\eta + 2.5\eta_d + (2\eta_{sh} + 3\eta_{dil})/a}{\eta + \eta_d + 0.4(2\eta_{sh} + 3\eta_{dil})/a}\Phi + O(\Phi^2). \qquad [3]$$

In Eq. [3], a denotes the droplet radius and η_{sh} and η_{dil} are the interfacial shear and dilatational viscosities, respectively.

The theoretical works of Einstein (1, 2), Taylor (3), and Oldroyd (9) have found development and applications in the rheology of disperse systems. In particular, Taylor (10), Fröhlich and Sack (11), and Oldroyd (12) applied asymptotic analysis to derive the next term in Eq. [2] with respect to the capillary number. Thus the effect of the droplet interfacial tension was included. This generalization may be important for very high shear rates. A second important generalization is to find appropriate expressions for the viscosity of suspensions containing particles with different shapes (13, 14). A third way of generalizing Eq. [1] is to calculate the next term in the series with respect to the volume fraction Φ. Batchelor (15) took into account the long-range hydrodynamic interaction between the particles to derive $\eta_{sus}/\eta = 1 + 2.5\Phi + 6.2\Phi^2 + \cdots$. From a mathematical viewpoint it is an exact result; however, from a physical viewpoint it is not entirely adequate for the real dispersions. The experimental results showed deviation from the Batchelor result, and for that reason a number of empirical expressions (16) have been proposed in which the coefficient multiplying Φ^2 varies between 5 and 15.

The development of new powerful numerical methods during the past 5 years has helped us achieve a better understanding of the rheology of emulsions (17–25). The simple shear and Brownian flow of dispersions of elastic capsules, rough spheres, and

liquid droplets were studied in Refs. (18, 22, 24, 25). The effects of insoluble surfactants and the drop deformation on the hydrodynamic interactions and on the rheology of dilute emulsions are the subjects of investigation in Refs. (19, 21, 23). Loewenberg and Hinch (17, 20) discussed the basic ideas of the numerical simulations of concentrated emulsion flows. These works are aimed at giving a theoretical interpretation of various experimental results for dilute and concentrated dispersions.

The main goal of the present work is to find a relatively simple expression for the viscosity of diluted emulsions taking into account all effects due to the presence of surfactants. In Section 2 the velocity and pressure distributions corresponding to the slow motion of an emulsion droplet subjected to a simple shear flow are studied. The Reynolds and Peclet numbers are assumed to be small enough to neglect the convective terms in the momentum balance and diffusion equations. The surfactants are soluble in both bulk phases, and the interface obeys a linear rheological law. In Section 3, using the standard procedure for averaging of the stress tensor flux, the exact formula for the viscosity of dilute emulsions is calculated. Finally, in Section 4, we summarize the conclusions. The results of this study can be used to quantify the effect of surfactant on the viscosity of diluted emulsions.

2. SLOW MOTION OF AN EMULSION DROPLET IN A SIMPLE SHEAR FLOW IN THE PRESENCE OF SURFACTANTS

We consider a simple shear viscous flow of continuous phase with viscosity η. The velocity at a large distance from the droplet is $\mathbf{v}_\infty$. The center O of the Cartesian coordinate system, Oxyz, and of the spherical coordinate system, O$r\theta\phi$, is located in the center of the droplet (see Fig. 1). In the Cartesian coordinate
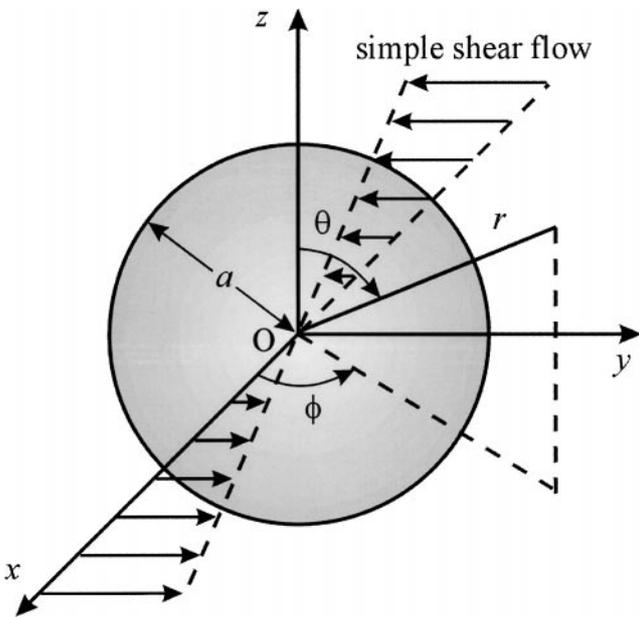

FIG. 1. Schematic picture of a viscous emulsion droplet in a simple shear flow.

system the velocity of the shear flow can be represented as $\mathbf{v}_\infty = (0, sx, 0)$, where s is the shear rate. For the bulk continuous phase we have to calculate the pressure, p, and the velocity, $\mathbf{v}$. The parameters characterizing the liquid in the droplets are denoted with subscript "d", viz. η_d, p_d, and $\mathbf{v}_d$. For small Reynolds numbers the mass and momentum balance equations are simplified to the well-known Stokes problem (13). In addition, we consider small emulsion droplets, which are spherical owing to the high capillary pressure. Therefore, the solution of the Stokes problem for the droplet phase is (13, 26)

$$p_d = p_\infty + \frac{2\sigma_e}{a} - 7s\eta_d A_1 \tilde{r}^2 \sin^2\theta \sin(2\phi), \tag{4a}$$

$$v_{d,r} = saA_1(\tilde{r} - \tilde{r}^3)\sin^2\theta \sin(2\phi), \tag{4b}$$

$$v_{d,\theta} = saA_1\left(\tilde{r} - \frac{5\tilde{r}^3}{3}\right)\sin\theta \cos\theta \sin(2\phi), \tag{4c}$$

$$v_{d,\phi} = saA_1\left(\tilde{r} - \frac{5\tilde{r}^3}{3}\right)\sin\theta \cos(2\phi) + saA_2\tilde{r}\sin\theta, \tag{4d}$$

where p_∞ is the pressure of the unperturbed flow at infinite distance from the droplet and σ_e is the unperturbed value of the interfacial tension (see the assumption for small Peclet number below). Likewise, for the continuous phase one derives

$$p = p_\infty - s\eta\frac{4A_1 + 5}{2\tilde{r}^3}\sin^2\theta \sin(2\phi), \tag{5a}$$

$$v_r = sa\left[\frac{\tilde{r}}{2} - \frac{5}{4\tilde{r}^2} + \frac{3}{4\tilde{r}^4} - A_1\left(\frac{1}{\tilde{r}^2} - \frac{1}{\tilde{r}^4}\right)\right]$$
$$\times \sin^2\theta \sin(2\phi), \tag{5b}$$

$$v_\theta = sa\left(\frac{\tilde{r}}{2} - \frac{1}{2\tilde{r}^4} - \frac{2A_1}{3\tilde{r}^4}\right)\sin\theta \cos\theta \sin(2\phi), \tag{5c}$$

$$v_\phi = sa\left(\frac{\tilde{r}}{2} - \frac{1}{2\tilde{r}^4} - \frac{2A_1}{3\tilde{r}^4}\right)\sin\theta \cos(2\phi)$$
$$+ sa\left(\frac{\tilde{r}}{2} - \frac{1}{2\tilde{r}^2} + \frac{A_2}{\tilde{r}^2}\right)\sin\theta. \tag{5d}$$

In Eqs. [4] and [5] the radial coordinate, r, is scaled with the droplet radius, $\tilde{r} \equiv r/a$, θ and ϕ are the polar and azimuthal angles, respectively (Fig. 1). For calculation of the solution the following boundary conditions are fulfilled. The velocity at infinity is $\mathbf{v}_\infty$. It is assumed that there is no mass transfer across the droplet interface—the radial component of the velocity at the interface is zero. The tangential components of the velocity at the interface are continuous and equal to the interfacial velocity, $\mathbf{u}$. Only the tangential stress boundary conditions can be used for determination of the unknown constants A_1 and A_2. The normal stress balance (equivalent to the Laplace equation of capillarity) simply states that the emulsion drops are spherical.

If the interface between two fluid phases, one of them being a surfactant solution, is disturbed, the equilibrium will be restored

either by exchange of surfactant between bulk and interface or by surface convection, driven by the gradient of interfacial tension, in interplay with the interfacial viscous friction. A linear rheological model of the interfacial dynamics is provided by the Boussinesq–Scriven constitutive law (26). The surfactant distribution affects the tangential stress boundary condition through the gradient of the interfacial tension. When the Peclet number is not small, the convective term in the bulk diffusion equation cannot be neglected and the respective problem has no analytical solution. Thus a complex numerical investigation has to be applied (27, 28).

We consider the general case of surfactant which is soluble in both liquid phases. We will assume that the relative motion of the emulsion droplets is so small that the Peclet number is a small parameter. The Peclet number is defined as follows: $\mathrm{Pe} \equiv s a^2 / D_{\mathrm{eff}}$, where D_{eff} is the effective diffusion coefficient given below in Eq. [10]. Therefore the assumption $\mathrm{Pe} \ll 1$ takes place when the droplet radius is small (in the order of several micrometers) or the shear rate, s, is small. Then, due to the flow, the surfactant concentrations, c and c_{d}, and the adsorption, Γ, slightly deviate from their equilibrium values, c_{e}, $c_{\mathrm{d,e}}$, and Γ_{e}:

$$c \equiv c_{\mathrm{e}} + c_{\mathrm{p}}, \quad c_{\mathrm{d}} \equiv c_{\mathrm{d,e}} + c_{\mathrm{d,p}}, \quad \Gamma \equiv \Gamma_{\mathrm{e}} + \Gamma_{\mathrm{p}}. \quad [6]$$

The subscript "p" denotes small perturbations. For stationary flows the adsorption process happens under diffusion control. The adsorption isotherm can be linearized by expansion in series around the equilibrium values of adsorption and concentrations. Thus from Eq. [6] one deduces

$$\Gamma_{\mathrm{p}} = h_{\mathrm{a}} c_{\mathrm{p}} = h_{\mathrm{d,a}} c_{\mathrm{d,p}} \quad \text{at } \tilde{r} = 1,$$
$$h_{\mathrm{a}} \equiv \left(\frac{\partial \Gamma}{\partial c}\right)_{\mathrm{e}}, \quad h_{\mathrm{d,a}} \equiv \left(\frac{\partial \Gamma}{\partial c_{\mathrm{d}}}\right)_{\mathrm{e}}, \quad [7]$$

where h_{a} and $h_{\mathrm{d,a}}$ denote the slopes of the adsorption isotherms. At small Peclet numbers the diffusion equation for the perturbation of the concentration in the bulk phase reduces to the Laplace equation (26). One can prove that only one mode of the spherical functions appears in the series, and the solution for the perturbations is

$$\Gamma_{\mathrm{p}} = \Gamma_{\mathrm{e}} A_3 \sin^2 \theta \sin(2\phi), \quad [8a]$$

$$c_{\mathrm{p}} = \frac{\Gamma_{\mathrm{e}}}{h_{\mathrm{a}}} \frac{A_3}{\tilde{r}^3} \sin^2 \theta \sin(2\phi),$$

$$c_{\mathrm{d,p}} = \frac{\Gamma_{\mathrm{e}}}{h_{\mathrm{d,a}}} A_3 \tilde{r}^2 \sin^2 \theta \sin(2\phi). \quad [8b]$$

The solution [8] obeys the following boundary conditions: (i) the linearized adsorption isotherm [7] and (ii) vanishing of the perturbation in the bulk concentration at a large distance from the surface of each droplet. The arbitrary constant, A_3, can be obtained from the surfactant mass balance at the interface.

In the case of stationary flows the surface convective and diffusion fluxes of adsorbed surfactant are compensated by the bulk diffusion fluxes of surfactant from the two adjacent phases. For small perturbations the surface convective flux can be linearized and the surface diffusion equation acquires the simpler form

$$\Gamma_{\mathrm{e}} \nabla_s \cdot \mathbf{u} - D_s \nabla_s^2 \Gamma_{\mathrm{p}} = D \frac{\partial c_{\mathrm{p}}}{\partial r} - D_{\mathrm{d}} \frac{\partial c_{\mathrm{d,p}}}{\partial r} \quad \text{at } \tilde{r} = 1. \quad [9]$$

Here ∇_s is the surface gradient operator, D_s is the surface diffusion coefficient, and D and D_{d} are the bulk diffusion coefficients of surfactants in the continuous and droplet phases, respectively. Substituting Eqs. [4], [5], and [8] into the boundary condition [9] one derives

$$\nabla_s \Gamma_{\mathrm{p}} = \frac{\Gamma_{\mathrm{e}}}{D_{\mathrm{eff}}} \mathbf{u}, \quad D_{\mathrm{eff}} \equiv D_s + \frac{a D}{2 h_{\mathrm{a}}} + \frac{a D_{\mathrm{d}}}{3 h_{\mathrm{d,a}}}. \quad [10]$$

It is seen that the effects of surface and bulk diffusion appear as a combined effective diffusion coefficient, D_{eff}. Equation [10] implies that for small perturbations the gradient of the interfacial tension becomes proportional to the surface velocity,

$$\nabla_s \sigma = \left(\frac{\partial \sigma}{\partial \Gamma}\right)_{\mathrm{e}} \nabla_s \Gamma_{\mathrm{p}} = -\frac{E_G}{D_{\mathrm{eff}}} \mathbf{u}, \quad E_G \equiv -\left(\frac{\partial \sigma}{\partial \ln \Gamma}\right)_{\mathrm{e}}, \quad [11]$$

where E_G is the surface (Gibbs) elasticity of the interface.

The form of the tangential stress boundary condition in spherical coordinates can be found in Ref. (26). Combining the latter equation with Eq. [11] we obtain

$$\frac{\eta_{\mathrm{d}}}{\eta} \tilde{r} \frac{\partial}{\partial \tilde{r}} \left(\frac{v_{\mathrm{d},\theta}}{\tilde{r}}\right) - \tilde{r} \frac{\partial}{\partial \tilde{r}} \left(\frac{v_{\mathrm{d},\theta}}{\tilde{r}}\right)$$
$$= \frac{\eta_{\mathrm{sh}}}{a\eta} \left\{ 2 u_\theta + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi} \left[\frac{\partial u_\theta}{\partial \phi} - \frac{\partial}{\partial \theta} (u_\phi \sin \theta) \right] \right\}$$
$$+ \frac{\eta_{\mathrm{sh}} + \eta_{\mathrm{dil}}}{a\eta} \frac{\partial}{\partial \theta} \left\{ \frac{1}{\sin \theta} \left[\frac{\partial u_\phi}{\partial \phi} + \frac{\partial}{\partial \theta} (u_\theta \sin \theta) \right] \right\}$$
$$- \frac{a E_G}{\eta D_{\mathrm{eff}}} u_\theta, \quad [12a]$$

$$\frac{\eta_{\mathrm{d}}}{\eta} \tilde{r} \frac{\partial}{\partial \tilde{r}} \left(\frac{v_{\mathrm{d},\phi}}{\tilde{r}}\right) - \tilde{r} \frac{\partial}{\partial \tilde{r}} \left(\frac{v_{\mathrm{d},\phi}}{\tilde{r}}\right)$$
$$= \frac{\eta_{\mathrm{sh}} + \eta_{\mathrm{dil}}}{a\eta} \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi} \left[\frac{\partial u_\phi}{\partial \phi} + \frac{\partial}{\partial \theta} (u_\theta \sin \theta) \right]$$
$$+ \frac{\eta_{\mathrm{sh}}}{a\eta} \left\{ 2 u_\phi - \frac{\partial}{\partial \theta} \left[\frac{1}{\sin \theta} \frac{\partial u_\theta}{\partial \phi} - \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (u_\phi \sin \theta) \right] \right\}$$
$$- \frac{a E_G}{\eta D_{\mathrm{eff}}} u_\phi. \quad [12b]$$

It should be noted that among all dependent variables Eqs. [12a, 12b] contain only the components of the velocity. As before, η_{sh} and η_{dil} denote the interfacial shear and dilatational viscosities.

Next, if the solutions for the velocity, Eqs. [4] and [5], are substituted into the boundary conditions, Eqs. [12a, 12b], the obtained linear system for the coefficients before each spherical function is solved and the following expressions for A_1 and A_2 are derived:

$$A_1 = -\frac{3}{4}\left[1 + \frac{\eta_d}{\eta} + \frac{2}{5}\left(\frac{aE_G}{2\eta D_{eff}} + \frac{3\eta_{dil} + 2\eta_{sh}}{a\eta}\right)\right]^{-1},$$

$$A_2 = \frac{1}{2}\left(1 + \frac{aE_G}{3\eta D_{eff}}\right)^{-1}. \qquad [13]$$

From the final form of the solution it is evident that there are only three independent dimensionless parameters related to the mobility of the interface. First, the ratio η_d/η is a measure of the magnitude of the dissipation of energy in the droplet phase. Second, the ratio $(3\eta_{dil} + 2\eta_{sh})/(a\eta)$ accounts for the influence of the surface viscosity. Third, the ratio $aE_G/(\eta D_{eff})$ compares the effects of surface elasticity, bulk viscosity, and the combined diffusivity. In particular, larger E_G corresponds to a more rigid interface. The increase of one of the diffusion coefficients leads to an increase of the surface velocity. A more detailed discussion is given in Section 3. In the limiting case $E_G \to 0$ Eqs. [4], [5], and [13] lead to the Oldroyd result (9).

3. INFLUENCE OF SURFACTANTS ON THE VISCOSITY OF DILUTE EMULSIONS

To derive the formula for the viscosity of emulsions in the dilute limit we will follow the way of calculation given in Ref. (29). The first step is the transformation of Eqs. [4], [5], and [13] into an invariant form, applicable to an arbitrary shear flow. The general form of the shear flow is defined by the shear-rate tensor $\mathbf{s}$, which has the following properties: it is symmetric, i. e., $s_{ik} = s_{ki}$, and the velocity of the shear flow, $v_{\infty,i} = s_{ik}x_k$, obeys the equation of continuity, i.e., $s_{kk} = 0$. Here and hereafter, we use the Einstein convention for summation over the repeating indices.

If the unit normal vector at the droplet surface is denoted by $\mathbf{n}$ (Fig. 2), then after transformation of the spherical coordinate system to any Cartesian coordinate system, $Ox_1x_2x_3$, we obtain the invariant form of Eqs. [4], [5], and [13]:

$$p_d = p_\infty + \frac{2\sigma_e}{a} + \frac{21}{2}\eta_d(1 - \varepsilon_m)\left(\frac{r}{a}\right)^2 n_j s_{jk} n_k, \qquad [14a]$$

$$v_{d,i} = -a(1 - \varepsilon_m)\left(\frac{r}{a}\right)^3 (n_j s_{jk} n_k)n_i$$
$$- \frac{3}{2}a(1 - \varepsilon_m)\left[\frac{r}{a} - \frac{5}{3}\left(\frac{r}{a}\right)^3\right]s_{ik}n_k. \qquad [14b]$$

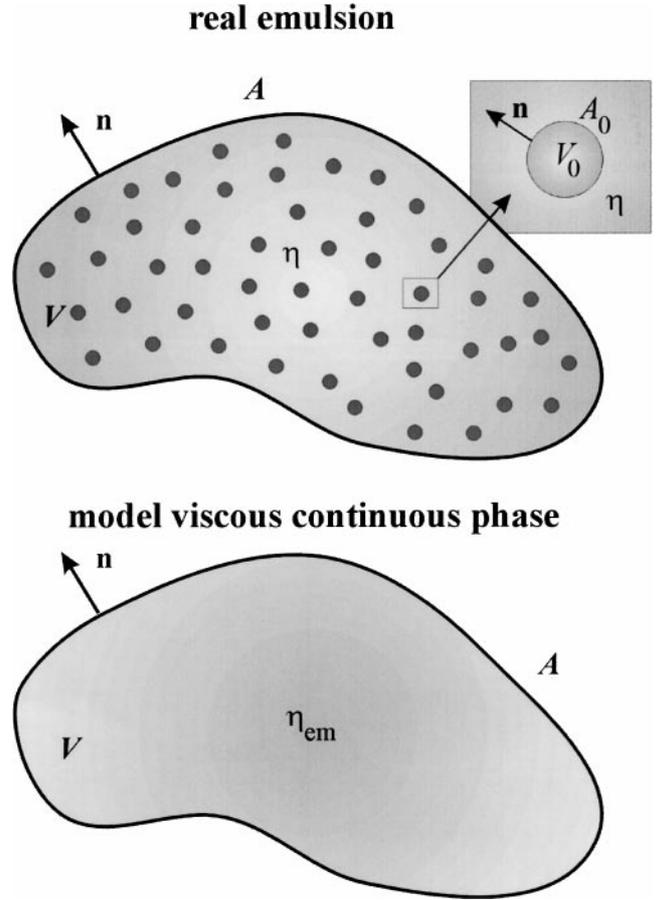$$p = p_\infty - \eta(3\varepsilon_m + 2)\left(\frac{a}{r}\right)^3 n_j s_{jk} n_k, \qquad [14c]$$

FIG. 2. Sketch of two identical control volumes from the real emulsion phase and from the model continuous phase.

$$v_i = s_{ik}x_k + \frac{a}{2}\left[5\varepsilon_m\left(\frac{a}{r}\right)^4 - (3\varepsilon_m + 2)\left(\frac{a}{r}\right)^2\right](n_j s_{jk} n_k)n_i$$
$$- a\varepsilon_m\left(\frac{a}{r}\right)^4 s_{ik}n_k. \qquad [14d]$$

All effects related to the drop viscosity and surfactant (bulk diffusion, surface elasticity, viscosity, and diffusivity) appear through the parameter ε_m, which is defined as follows:

$$\varepsilon_m \equiv \left(\frac{\eta_d}{\eta} + \frac{2}{5}\left(\frac{aE_G}{2\eta D_{eff}} + \frac{3\eta_{dil} + 2\eta_{sh}}{a\eta}\right)\right)\bigg/\bigg(1 + \frac{\eta_d}{\eta}$$
$$+ \frac{2}{5}\left(\frac{aE_G}{2\eta D_{eff}} + \frac{3\eta_{dil} + 2\eta_{sh}}{a\eta}\right)\bigg) \qquad [15]$$

This parameter accounts for the tangential mobility of the droplet interface; note that $0 \le \varepsilon_m \le 1$. In the limiting case $E_G \to \infty$, Eq. [15] yields $\varepsilon_m = 1$ (immobile interface). The other special case $\eta_d \to 0$ (gas bubble) and the surfactant free interface ($E_G \to 0$, $\eta_{dil} \to 0$, $\eta_{sh} \to 0$) correspond to $\varepsilon_m = 0$ (completely mobile interface).

The second step is to calculate the total (integral) stress acting on the surface A of a control volume V (Fig. 2). The surface of V is chosen to be away from any emulsion droplet. In dilute emulsions the distances between the droplets are sufficiently large. For that reason, the droplets do not interact with each other—they disturb only the flow of the continuous phase. The stress tensor of the continuous phase of the real emulsion is

$$P_{ik} = \eta\left(\frac{\partial v_{\infty i}}{\partial x_k} + \frac{\partial v_{\infty k}}{\partial x_i}\right) - p_\infty \delta_{ik}$$

$$+ \sum\left[\eta\left(\frac{\partial v_{pi}}{\partial x_k} + \frac{\partial v_{pk}}{\partial x_i}\right) - p_p \delta_{ik}\right]. \quad [16a]$$

The summation in Eq. [16a] is over all droplets in the control volume, and $\mathbf{v}_p \equiv \mathbf{v} - \mathbf{v}_\infty$ and $p_p \equiv p - p_\infty$ are the perturbations of the shear flow parameters from each individual droplet calculated in Section 2. The model continuous fluid occupies the same control volume and performs the same shear flow, but it has different viscosity, η_{em}. Therefore, the stress tensor of the model phase is

$$P_{\text{mod},ik} = \eta_{em}\left(\frac{\partial v_{\infty i}}{\partial x_k} + \frac{\partial v_{\infty k}}{\partial x_i}\right) - p_\infty \delta_{ik}. \quad [16b]$$

To make the model system mechanically equivalent to the real emulsion, we require the work per unit of time produced by the exerted stresses to be the same (see Refs. (13, 29)):

$$W \equiv \oiint_A v_{\infty i} P_{ik} n_k \, dA = \oiint_A v_{\infty i} P_{\text{mod},ik} n_k \, dA \equiv W_{\text{mod}}. \quad [17]$$

Here $\mathbf{n}$ is the running unit normal to the surface of the control volume (Fig. 2).

From Eqs. [16b] and [17] we deduce

$$W_{\text{mod}} = 2\eta_{em} s_{ik} s_{ki} V. \quad [18a]$$

On the other hand, an expression for W can be derived after longer mathematical transformations: Eq. [16a] is substituted into the definition [17]; the surface integral over A is transformed to a sum of an integral over the volume of the continuous phase and over the surfaces of the droplets (Fig. 2) using the Gauss–Ostrogradsky theorem. The final result reads

$$W = 2\eta s_{ik} s_{ki} V + \eta \sum (7\varepsilon_m - 2) a^3 s_{ij} s_{ik}$$

$$\times \int_0^{2\pi} \int_0^\pi n_j n_k \sin\theta \, d\theta \, d\phi$$

$$- \eta \sum (10\varepsilon_m - 1) a^3 s_{ij} s_{kl} \int_0^{2\pi} \int_0^\pi n_i n_j n_k n_l \sin\theta \, d\theta \, d\phi. \quad [18b]$$

The first double integral in Eq. [18b] gives $4\pi \delta_{jk}/3$, and the second double integral has the simple form $4\pi(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})/15$. Combining Eqs. [17], [18a], and [18b] we obtain

$$\eta_{em} s_{ik} s_{ki} V = \eta s_{ik} s_{ki} V + \eta s_{ik} s_{ki} \sum \frac{4\pi a^3}{3}\left(1 + \frac{3\varepsilon_m}{2}\right). \quad [19]$$

Equation [19] has to be fulfilled for each control volume and shear rate; thus one obtains the following expression for the effective viscosity of the emulsion, η_m,

$$\frac{\eta_{em}}{\eta} = 1 + \left(1 + \frac{3}{2}\langle\varepsilon_m\rangle\right)\Phi + O(\Phi^2), \quad \langle\varepsilon_m\rangle \equiv \frac{\sum a^3 \varepsilon_m}{\sum a^3}, \quad [20]$$

where $\langle\varepsilon_m\rangle$ is the average value of the interfacial mobility parameter for all droplets in the control volume (as before, a denotes the droplet radius). If the droplet size distribution in the emulsion and the interfacial rheological parameters are known then the average value $\langle\varepsilon_m\rangle$ can be estimated. For monodisperse emulsions the average value, $\langle\varepsilon_m\rangle$, and the interfacial mobility parameter, ε_m, are equal. In the special case of completely mobile interfaces, that is, $a E_G/(\eta D_{\text{eff}}) \to 0$ and $(3\eta_{\text{dil}} + 2\eta_{\text{sh}})/(a\eta) \to 0$, the mobility parameter, ε_m, does not depend on the droplet size, and from Eqs. [15] and [20] the Taylor formula, Eq. [2], is obtained. It is important to note that the Taylor formula takes into account only the bulk properties of the phases (characterized by η_d/η); in such a case ε_m is independent of a and therefore Eq. [2] is applicable also to polydisperse emulsions. If only the Marangoni effect is neglected ($E_G \to 0$), then Eqs. [15] and [20] become equivalent to the Oldroyd formula. The original result of Oldroyd is valid only for monodisperse emulsions (15). In general, due to the combination of bulk and interfacial fluxes, the mobility parameter, ε_m, depends on the droplet radius a; see Eq. [15].

It is interesting to estimate the contributions of the different terms in Eq. [15]. The ratio between the interfacial viscous and elastic stresses is characterized by

$$\frac{\text{surface viscous term}}{\text{surface elastic term}} = 2D_{\text{eff}}\frac{3\eta_{\text{dil}} + 2\eta_{\text{sh}}}{a^2 E_G}. \quad [21]$$

If typical values of the interfacial rheological parameters (30) for nonionic and ionic surfactants, or protein isolates, are substituted in Eq. [21], one can conclude that the ratio in Eq. [21] is always smaller than 1 or of the order of 1. Therefore, the surface elastic effects in [20] cannot be neglected.

The ratio of the contributions from the surface elastic stresses and the bulk viscous stresses is given by

$$\frac{\text{surface elastic term}}{\text{bulk friction term}} = \frac{E_G}{5\eta}\left(\frac{D_s}{a} + \frac{D}{2h_a} + \frac{D_d}{3h_{d,a}}\right)^{-1}. \quad [22a]$$

This ratio depends on the type of surfactant and on the diffusion coefficients. For insoluble monolayers the bulk diffusion terms

have to be omitted and Eq. [22a] reduces to

$$\frac{\text{surface elastic term}}{\text{bulk friction term}} = \frac{aE_G}{5\eta D_s} \quad \text{(insoluble monolayers).}$$

[22b]

Practically for all insoluble monolayers this ratio has very large values, and therefore, the interfaces are tangentially immobile owing to the surface elasticity (rather than to the surface viscosity), cf. Eq. [21]. For conventional surfactants the slope of the isotherm (in the order of several nm) is much smaller than the droplet size in the emulsion (in order of several μm). Therefore, the ratio [22a] can be estimated as

$$\frac{\text{the Marangoni term}}{\text{the bulk friction term}} \approx \frac{2h_aE_G}{5\eta D} \quad \text{(conventional surfactants).}$$

[22c]

Because of the not so big difference between the surface and bulk diffusion coefficients, if we compare Eqs. [22b] and [22c] we can conclude that the droplet interfaces can be mobile in the case of low molecular weight surfactants or microemulsions. Then the viscosity of such emulsions is lower than the Einstein formula [1] predicts and higher than that calculated from the Taylor formula [2].

4. CONCLUSIONS

The exact analytical solution of the problem for the slow motion of a liquid droplet in a shear flow is derived; see Section 2. The surfactant is assumed to be soluble in both phases, and the interface obeys the linear Boussinesq–Scriven constitutive law. The assumption of small Reynolds and Peclet numbers for the flow allows us to use the linear form of the surfactant adsorption isotherm for small deviations of the concentration and adsorption from the equilibrium state. The influence of the interfacial viscosity, Gibbs elasticity, and surface and bulk diffusion of surfactant on the tangential mobility of the droplet interface is discussed.

Imposing the condition for equivalence of the real and model systems (Fig. 2) with respect to the mechanical work per unit of time, an expression for the viscosity of dilute emulsions in the presence of surfactants is derived. If the size distribution of the droplets and the interfacial properties of the system are known, the effective viscosity of the emulsion can be calculated, see Eqs. [15] and [20]. The relative importance of the surface elasticity and viscosity is discussed in Section 3. It is shown that (depending on the type of surfactant) either the two effects have

the same order of magnitude or the surface elasticity is more important than the surface viscosity for the tangential mobility of interfaces and for its impact on the viscosity of the emulsion.

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