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EFFECTIVE VISCOSITY OF AN EMULSION IN A SURFACTANT SOLUTION

A. Yu. Zubarev and Yu. V. Shilko

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A surfactant affects the effective viscosity of an emulsion because of capillary phenomena in shear flow. The surfactant gives the emulsion non-Newtonian behavior.

A surfactant affects emulsion rheology [1] and in particular increases the effective viscosity. The usual explanation for this is that surfactant layers are formed around the droplets whose surface viscosity is different from the bulk viscosity of the liquids inside and outside them (see [1] and references in that review to the primary sources). Here we give another explanation based on [2], namely droplet fall in surfactant solutions.

Consider a droplet in a flowing liquid containing a dissolved surfactant, which is adsorbed on it and thus reduces the surface tension. The convective surfactant flow alters the concentration at the surface, so the interfacial tension varies over the surface, and tangential capillary stresses arise that entrain the liquid on both sides in the additional flows introduced by the droplet in the external flow. This increases the flow energy dissipation by comparison with no surfactant. This means that the effective viscosity is increased in a system containing many such droplets.

Here we estimate the viscosity from such concepts, where for simplicity we assume that all the droplets are identical and the surface tension is sufficient to retain the spherical shape.

The effective viscosity η for a suspension of identical spheres can be derived from many equivalent formulas [3-6]; for definiteness, we use the one given in [6]:

$$(\eta-\eta_0)\,e_{ij}=\frac{3a^3}{4\pi}\,\rho\Big[\int\limits_{r=a} r_i n_l \sigma_{lj}^{+} d\mathbf{r}-\eta_0\int\limits_{r=a}(n_i v_j^{+}+n_j v_i^{+})\,d\mathbf{r}\Big],\ i,\ j,\ l=x,\ y,\ z, \tag{1}$$

where summation with respect to the repeating subscripts is understood.

The integration is over some arbitrarily selected drop. To calculate the integrals in (1), one needs to know the stress $\boldsymbol{\sigma}^{+}$ and velocity $\mathbf{v}^{+}$ of the flow at the outer boundary. In general, this involves considering many other particles, which is extremely complicated; the soundest study appears to be in [6]. To concentrate attention on principles, we consider a very dilute system, where each droplet can be considered in isolation.

Gor'kii Ural University, Sverdlovsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 54, No. 5, pp. 752-759, May, 1988. Original article submitted February 13, 1987.

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In the quasistationary approximation, and with inertial terms neglected, the flow structure near any drop is defined by

$$\begin{gathered}\nabla p^{+}+\eta_0\Delta\mathbf{v}^{+}=0,\quad \operatorname{div}\mathbf{v}^{+}=0,\quad r\geqslant a;\quad \nabla p^{*}+\eta_1\Delta\mathbf{v}^{*}=0,\\ \operatorname{div}\mathbf{v}^{*}=0,\quad r\leqslant a;\quad \mathbf{v}^{+}\to\mathbf{v},\quad r\to\infty;\quad v^{*}<\infty,\quad r=0;\\ v_n^{+}=0,\quad \overset{*}{v}_n=0,\quad v_t^{+}=\overset{*}{v}_t,\quad \sigma_{nt}^{+}+\operatorname{grad}_s\tau=\overset{*}{\sigma}_{nt},\quad -p^{+}+\sigma_{nn}^{+}=-p^{*}+\overset{*}{\sigma}_{nn},\\ r=a;\quad \boldsymbol{\sigma}^{+}=2\eta_0\mathbf{e}^{+},\quad \boldsymbol{\sigma}^{*}=2\eta_1\mathbf{e}^{*}.\end{gathered}\tag{2}$$

Here v is the mean velocity of this mixture as a whole, with $\operatorname{grad}_S\tau$ the tangential capillary stress at the droplet [2]; grad_S is a surface gradient calculated in the same way as the usual one but for specified values of the radius vector here equal to the droplet radius a. In accordance with [2], we rewrite the expression for the capillary stress:

$$\operatorname{grad}_s\tau=\frac{\partial\tau}{\partial\Gamma}\operatorname{grad}_s\Gamma.\tag{3}$$

Then (2) can be solved if one knows the surface surfactant concentration Γ at the droplet and how the interfacial tension τ varies with Γ; Γ is determined by the adsorption and desorption conditions. For definiteness we assume that Langmuir's law applies and that the surface diffusion for the surfactant in the droplet can be neglected, as is commonly the case.

Then the surfactant distribution near the drop is

$$\begin{gathered}\frac{\partial C^{+}}{dt}+\mathbf{v}^{+}\nabla C^{+}=D_0\Delta C^{+},\quad r\geqslant a;\\ -D_0\frac{\partial C^{+}}{\partial r}+\alpha(1-s\Gamma)C^{+}-\beta\Gamma=\operatorname{div}_s\Gamma v_t^{+},\ r=a;\ C^{+}\to C^{0},\ r\to\infty,\end{gathered}\tag{4}$$

where div_S is the surface-divergence operator, which is defined as usual for $r\equiv a$.

The first term on the left in the boundary condition in (4) is the usual diffusion flux, while the second and third terms are the amounts of surfactant adsorbed and desorbed by unit surface in unit time in accordance with Langmuir's law. On the right, we have the surface convective surfactant flux at the droplet [2].

From (2)-(4) one can in principle derive v^{+} for a given mean v, equilibrium surfactant concentration C^0 in solution, and the parameters characterizing the viscosities of the dispersed and dispersing liquids, the surfactant diffusion, and the adsorption and desorption.

Grave mathematical difficulties arise in solving (2)-(4) exactly, and here we consider limiting cases, where the Peclet number $\mathrm{Pe}=va/D_0$ is very small or very large.

Small Peclet Numbers ($\mathrm{Pe}\ll 1$). We linearize (2)-(4) in Pe as

$$C^{+}=C^{\circ}+c,\quad \Gamma=\Gamma^{\circ}+\gamma;\ C^{\circ},\ \Gamma^{\circ}=\text{const},\ \left\{\frac{c}{C^{\circ}},\ \frac{\gamma}{\Gamma^{\circ}}\right\}\sim\mathrm{Pe}.$$

Then (3) becomes

$$\operatorname{grad}_s\tau=\frac{\partial\tau}{\partial\Gamma^{\circ}}\operatorname{grad}_s\gamma,\tag{5}$$

with the relation between γ and c

$$\gamma=\frac{\partial\Gamma^{\circ}}{\partial C^{\circ}}c(a),\tag{6}$$

and (4) becomes

$$\begin{gathered}\frac{\partial c}{\partial t}=D_0\Delta c,\quad r\geqslant a;\quad -D_0\frac{\partial c}{\partial r}+Mc=\Gamma^{\circ}\operatorname{div}_s v_t^{+},\ r=a;\ c\to 0,\ r\to\infty;\\ M=-\frac{\partial\Gamma^{\circ}}{\partial C^{\circ}}(\beta+\alpha sC^{\circ})+\alpha(1-s\Gamma^{\circ}),\quad \Gamma^{\circ}=\frac{\alpha C^{\circ}}{\beta+\alpha sC^{\circ}}.\end{gathered}\tag{7}$$

To determine η from (1), we assume that the drop is introduced into a pure shear flow defined as

$$v_x = ex; \quad v_y = -ey; \quad v_z = 0, \tag{8}$$

where x, y, and z are cartesian coordinates in a system having its center within the drop, while v_x, v_y, and v_z are the corresponding flow-rate coordinates. The final results are not affected by the form given for v in (8), but the calculations are much facilitated.

We take a spherical coordinate system having its origin at the center of the drop and its polar axis along the z axis, the polar and azimuthal angles being θ and φ. We write the components of v in (8) in this system in accordance with the usual rules [7] and solve (2) as

$$\begin{gathered} v_r^+ = (A_{-2}r^{-2} + A_{-4}r^{-4} + er)\,Y_r, \quad v_\theta^+ = \left(-\frac{2}{3}A_{-4}r^{-4} + er\right)Y_\theta, \\ v_r^* = (A_1 r + A_3 r^3)\,Y_r, \quad v_\theta^* = \left(A_1 r + \frac{5}{3}A_3 r^3\right)Y_\theta, \\ v_\varphi^+ = -v_\theta^+\frac{Y_\varphi}{Y_\theta}, \quad v_\varphi^* = -v_\theta^*\frac{Y_\varphi}{Y_\theta}, \\ Y_r = \sin^2\theta\cos 2\varphi, \quad Y_\theta = \sin\theta\cos\theta\cos 2\varphi, \quad Y_\varphi = \sin\theta\sin 2\varphi, \end{gathered} \tag{9}$$

where A_j are constants of integration, which must be derived from (2) with (3) and (5)-(7).

Fourier time transformations can be used in solving (7), so ∂/∂t is replaced by i_ω ($i = \sqrt{-1}$). We use the representations for v_θ^+, v_φ^+ in (7) chosen from (9) and derive c(r) as

$$c(\mathbf{r}) = GH_2(\varkappa r)\,r^{-1/2}Y_r, \quad \varkappa = \sqrt{i\frac{\omega}{D_0}},$$

where G is a constant of integration and H_2 is a Hankel function of the first kind. G is derived from (7), and then (6) gives

$$\begin{gathered} \frac{\partial\tau}{\partial\Gamma^\circ}\gamma = Bq\left(ea - \frac{2}{3}A_{-4}a^{-4}\right)Y_r, \quad B = -\frac{3\Gamma^\circ}{a}\,\frac{\partial\Gamma^\circ}{\partial C^\circ}\,\frac{\partial\tau}{\partial\Gamma^\circ}, \\ q = \frac{h}{D_0 f + Mh}, \quad f = -\frac{}{\partial a}{}_2(\varkappa a)H[\varrho\, a^{-1/2}], \quad h = H_2(\varkappa a)\,a^{-1/2}. \end{gathered} \tag{10}$$

We substitute (10) into (5) and then these with (9) into (2) to get A_{-2} and A_{-4}, which we use in (9) and (1) to get the effective viscosity as

$$\eta = \eta_0\left[1 + \frac{\eta_0 + \frac{5}{2}\left(\eta_1 + \frac{3}{10}Bq\right)}{\eta_0 + \eta_1 + \frac{3}{10}Bq}\,\rho\right], \tag{11}$$

where B and q are defined in (10). If there is no adsorption (B = 0), (11) becomes the classical Taylor formula.

The (10) definition for q shows that η is very much dependent on ω. To examine nonharmonic nonstationary processes, we write

$$\sigma = 2\eta\mathrm{e}. \tag{12}$$

We substitute (11) into (12) and use inverse Fourier transformations to get a complicated integrodifferential time-dependent relation between σ and the shear rate **e**. Consequently, an emulsion in a surfactant solution has non-Newtonian behavior.

The **σ–e** relation simplifies substantially for slightly nonstationary processes, where $\omega a^2/D_0 \ll 1$. We expand η from (11) in powers of $\varkappa a$, as

$$\eta \approx \eta^\circ[1 + T_1 i\omega + T_2^{3/2}(i\omega)^{3/2} + \ldots], \tag{13}$$

$$\eta^\circ = \eta_0 \left[1 + \frac{\eta_0 + \frac{5}{2}\left(\eta_1 + \frac{3}{10} Bq^\circ\right)}{\eta_0 + \eta_1 + \frac{3}{10} Bq^\circ} \rho \right], \tag{13}$$
$$q^\circ = q(\omega = 0) = a(3D_0 + Ma)^{-1},$$

where η^0 is the stationary value for the effective viscosity for Pe ≪ 1, while the times T_1 and T_2 are readily derived from (10) with (11) along with explicit expressions for the Hankel functions [7]. To abbreviate the formulas, T_1 and T_2 are not given explicitly, and we merely state that $T_j \sim (a^2/D_0)\rho$ as regards order of magnitude. We substitute (13) into (12) and use inverse Fourier transformations to get

$$\sigma(t) \approx 2\eta^\circ \left[\mathbf{e}(t) + T_1 \frac{\partial \mathbf{e}(t)}{\partial t} + \frac{T_2^{3/2}}{\sqrt{\pi}} \int\limits_{-\infty}^{t} \frac{dt'}{\sqrt{t - t'}} \frac{\partial^2 \mathbf{e}(t')}{\partial t'^2} \right]. \tag{14}$$

It follows from (14) that the relation between $\boldsymbol{\sigma}$ and $\mathbf{e}$ acquires a relaxation form and then an inherited one as the flow becomes more nonstationary.

The physical reason for the time-dependent effects in (14) is that each $\mathbf{e}$ corresponds to a particular stationary distribution $C^+(\mathbf{r})$ near the drop; however, when $\mathbf{e}$ varies, this is attained not instantaneously but in a time of order a^2/D_0.

We now estimate the characteristic times T_j in (14); $D_0 \sim 10^{-10}$ m²/sec for many aqueous surfactant solutions, while $T_j \sim (a^2/D_0)\rho$ implies that $T_j \sim 10^{-1}\rho$ sec for an emulsion containing micron droplets. Therefore, relaxation effects will occur for nonstationary processes whose characteristic times are 10^{-2} sec or less, which coincides with acoustic-wave periods. $T_j \sim 10^4\rho$ sec for millimeter drops, so relaxation effects should occur here with quite slow flows, whose characteristic times may be minutes or even hours.

Large Peclet Numbers (Pe ≫ 1). Here (4) cannot be linearized with respect to the velocity and there are major mathematical difficulties. Some methods have been developed [8], but the final results ae cumbersome and the analysis is extremely difficult. To obtain clear-cut formulas allowing physical analysis, we use a simple model for a diffusion boundary layer, in which each drop is taken as surrounded by a concentric layer, thickness δ ($\delta \ll a$), and outside it, i.e., for $r > a + \delta$, one can neglect the diffusion term in the first equation in (4), while within it ($a < r < \delta + a$), the velocity is taken as small and one can linearize with respect to it. Also, we first consider stationary processes.

It can be shown from the first equation in (4) that $C^+ = C^0$ for $r > \delta + a$. We expand C^+ and Γ in the second equation in (4) in powers of the small parameter $v_t^+(a)a/D_0$, and in the linear approximation get

$$C^+ = C^\circ + c, \ \Gamma = \Gamma^\circ + \gamma, \ \left\{\frac{c}{C^\circ}, \frac{\gamma}{\Gamma^\circ}\right\} \sim \frac{v^+(a)\,a}{D_0}, \ a < r < \delta + a. \tag{15}$$

We use (9) and (15) in (4) on the basis that $\delta \ll a$, $\partial c/\partial r \sim -c/\delta$ to get

$$c(a) = \frac{3\Gamma^\circ}{a}\left(ea - \frac{2}{3} A_{-4} a^{-4}\right)\left(\frac{D_0}{\delta} + M\right)^{-1} Y_r, \tag{16}$$
$$\gamma = \frac{\partial \Gamma^\circ}{\partial C^\circ} c(a), \quad \Gamma^\circ = \frac{\alpha C^\circ}{\beta + \alpha s C^\circ}.$$

We use (15) and write $\mathrm{grad}_s \tau$ in (2) as in (5). We substitute (9) into (2) and use (5) and (16) to get $\mathbf{v}^+$ near the drop. Then we use the standard method [3] to calculate $\boldsymbol{\sigma}^+$ and substitute for $\mathbf{v}^+$ and $\boldsymbol{\sigma}^+$ in (1), which gives a formula for the effective viscosity coincident with (11) but with

$$q = \frac{\delta}{D_0 + M\delta}, \tag{17}$$

while B is as in (10).

We have to estimate δ to use (11) and (17); arguments similar to those in [2] show that for $Bq \ll \eta_0$

$$\delta \sim \left(\frac{D_0}{\|\mathbf{e}\|} \right)^{1/2}. \tag{18}$$

and for $Bq \gg \eta_0$

$$\delta \sim \left(\frac{D_0 a}{\|\mathbf{e}\|} \right)^{1/3}. \tag{19}$$

where $\|\mathbf{e}\|$ is the root from the sum of the squares of the diagonal elements in tensor $\mathbf{e}$ written in terms of the principal axes. In general, $\delta \sim \|\mathbf{e}\|^{-m}$, where $1/3 < m < 1/2$, but a separate study is needed to define $\delta(\|\mathbf{e}\|)$ for arbitrary Bq/η_0.

We now substitute (17) into (11) and further into (12) to get a formula relating the mean stress tensor $\boldsymbol{\sigma}$ and shear rate $\mathbf{e}$:

$$\boldsymbol{\sigma} = 2\eta_0 \left\{ 1 + \frac{\eta_0 + 2.5\left[\eta_1 + Bg\|\mathbf{e}\|^{-m}(D_0 + Mg\|\mathbf{e}\|^{-m})^{-1}\right]}{\eta_0 + \eta_1 + Bg\|\mathbf{e}\|^{-m}(D_0 + Mg\|\mathbf{e}\|^{-m})^{-1}}\,\rho \right\} \mathbf{e}, \qquad \frac{1}{3} < m < \frac{1}{2}, \tag{20}$$

where g is a coefficient of proportionality between δ and $\|\mathbf{e}\|^{-m}$, which is estimated in (18) and (19) for the two limiting cases. Then the surfactant for $Pe \gg 1$ produces non-Newtonian behavior different from that for $Pe \ll 1$: there is a nonlinear relation between $\boldsymbol{\sigma}$ and $\mathbf{e}$.

For $Pe \ll 1$, the relation between σ and e in (14) is of relaxation or inherited types; it is readily shown that this feature disappears for $Pe \gg 1$. If we consider (4) in the previous boundary-layer approximation, we see that there is a solution $C^+ = C^0 = \text{const}$ in the region $r > \delta + a$ for any $v(t)$, and then from (2) and (4) we again get in sequence (16) and then (11) and (17). It can be shown that any other solutions to the first equation in (4) derived on neglecting the diffusion part do not contribute to the integrals in (1), so increasing the flow speed eliminates time-dependent effects of (14) type.

We can compare (11), (13), and (20) with the theory in which the surfactant at the drop is incorporated by means of the empirical surface viscosity η_s. We use (IV.221) from [1], which can be written as

$$\eta = \eta_0 \left[1 + \frac{\eta_0 + \frac{5}{2}(\eta_1 + \eta_s/a)}{\eta_0 + \eta_1 + \eta_s/a}\,\rho \right].$$

This coincides formally with (11) if $3Bq/10$ is replaced by η_s/a. However, while in [1] and similar papers, η_s was taken as constant and derived empirically, (11), (13), and (20) have been derived from first principles and not merely establish the relation of Bq to surfactant diffusion and adsorption, as well as droplet size, but also indicate that the effective viscosity is dependent on the flow frequency and velocity.

Equations (11) and (20) imply that for $Bq/\eta_0 \sim \infty$, which is so for sufficiently large Γ, the effective viscosity tends to

$$\eta = \eta_0(1 + 2.5\rho), \tag{21}$$

which coincides with that for a dilute suspension of hard spheres derived from Einstein's formula. Droplet solidification at high surfactant surface concentrations occurs [1] and has been ascribed to elevated surface viscosities. In our model, this is explained as follows. It follows from (5) and (10) that the surface capillary stress preventing the drop from being deformed by the flow is of the order of Bqe_{ij}. The order of the hydrodynamic stress in the carrying liquid is $\eta_0 e_{ij}$, so the external flow cannot deform the drop for $Bq \gg \eta_0$ and thus excite circulating flows within it. The drop exerts an effect on the flow the same as for a hard sphere having the same radius. Therefore, the viscosity of an emulsion for $Bq/\eta_0 \to \infty$ is the same as that of a hard-sphere suspension having the same ρ.

The largest change in effective viscosity will occur in a system in which the viscosity in the drop is much less than that of the dispersing liquid. We compare the limiting situations in (11) where $\eta_1 \ll \eta_0$, $Bq = 0$ (surfactant absent), which leads to $\eta = \eta_0(1 + \rho)$, with

(21), which applies for $Bq/\eta_0 \to \infty$ (surfactant concentration at drop large), which shows that $(\eta - \eta_0)/\eta_0$ can increase by a factor 2.5ρ as the surfactant concentration increases. A drop behaves as a hard sphere in a concentrated surfactant solution, as is familiar from the experiments discussed in [2].

The derivative $\partial\tau/\partial\Gamma^0$ appearing in the expression for B in (11) is readily derived from thermodynamic arguments [2, 9] as

$$\frac{\partial\tau}{\partial\Gamma^\circ} = -RT\frac{\Gamma^\circ}{C^\circ}\frac{\partial C^\circ}{\partial\Gamma^\circ},$$

where R and T are the universal gas constant and the absolute temperature, while the Γ^0 dependence of C^0 can be derived from (7) and (16).

NOTATION

a, droplet radius; C^0, equilibrium surfactant concentration in solution; C^+, surfactant concentration near drop; $c = C^+ - C^0$; D_0, surfactant diffusion coefficient in main liquid; $\mathbf{e}$ and e_{ij}, shear flow velocity tensor and component of this; M, defined in (7); n_i, component of unit normal to droplet surface; p, pressure; q, defined in (10) and (17); $\mathbf{r}$, radius vector with origin at droplet center; s, proportion of droplet surface occupied by one surfactant molecule; $\mathbf{v}$, flow speed; t, time; Y_r, Y_θ, and Y_φ, defined in (9); α and β, sorption and desorption constants; Γ, surface surfactant concentration on drop; Γ^0, equilibrium Γ; $\gamma = \Gamma - \Gamma^0$; δ, boundary-layer thickness; η, viscosity; ρ, volume droplet concentration; σ and σ_{ij}, hydrodynamic-stress tensor and component of this; τ, droplet surface tension; ω, Fourier frequency. Superscripts and subscripts: 0 and 1, main and dispersed liquids; n and t, normal and tangential components for vectors and tensors at droplet surface; + and $*$, quantities inside and outside droplet; and σ, $\mathbf{e}$, $\mathbf{v}$, and η, without subscripts or superscripts refer to the mixture as a whole.

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