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## NON-NEWTONIAN PROPERTIES OF EMULSIONS IN SOLUTIONS OF SURFACE-ACTIVE AGENTS

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The adsorption of surface-active agents (surfactants) on channels changes the effective viscosity of an emulsion and gives it non-Newtonian properties.

Establishing the form of rheological equations of state of disperse systems is one of the most important problems in the physical mechanics of mixtures. This problem is far from being resolved even for the simplest systems - suspensions of rigid particles or Newtonian drops in a Newtonian fluid. The situation is even more complicated if physicochemical processes which alter the structure of the flow near the particle are taking place on the surface of a particle or drop. Such phenomena can have a significant effect on the behavior of the mixture as a whole. Meanwhile, the result of this effect is impossible to predict by means of a phenomenological modeling of continuum equations.

Here, we study the rheological properties of emulsions whose drops might adsorb an impurity contained in the dispersion medium. It was shown in [1] that the capillary effects which occur in this case impart non-Newtonian properties to the emulsion even when the disperse phase and the dispersion medium are Newtonian fluids. However, it was assumed in [1] that sorption-desorption processes take place at an infinitely high rate. Below, we consider the finiteness of these processes. At the same time, we correct the errors allowed in [1]. As in [1], we examine limitingly dilute mixtures in which we can ignore any particle interaction. The surface tension of the drops is assumed to be strong enough to ensure that they are spherical in form during the flow process.

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In a continuum approximation, the connection between the mean tensors of hydrodynamic stress  $\sigma$  and the rate of shear flow  $e$  can be formally written in the usual form

$$\sigma = 2\eta e, \quad (1)$$

where  $\eta$  is, generally speaking, a nonlinear operator with respect to the coordinates and time. It is determined from the relation [2]

$$2(\eta - \eta_0) e_{ij} = \frac{3a^3}{4\pi} \rho \left[ \int_{|r|=a} r_i n_l \sigma_{lj}^+ dr - \eta_0 \int_{|r|=a} (n_i v_j^+ + n_j v_i^+) dr \right], \quad (2)$$

$$i, j, l = x, y, z$$

(summation is performed over the repeating indices). Here, we integrate over the surface of an arbitrarily-chosen drop. In the general case, when determining the stress  $\sigma^+$  and the velocity  $v^+$  on the surface of the drop, it is necessary to account for the presence of the remaining particles of the mixture. This multiparticle problem is one of the most complex in the physical mechanics of mixtures and is presently very far from resolution. In limitingly dilute systems ( $\rho \ll 1$ ) - the only type of systems we will consider here - the mutual effect of the particles can be ignored and we can assume that a drop is located in an infinite volume of the dispersion medium. We can also assume that the flow velocity at an infinite distance from the drop coincides with the mean velocity of the emulsion in the region being examined. We will assume that this velocity is completely described by the mean tensor  $e$ .

The continuum approximation is valid if the linear scales of change in flow velocity and pressure are much greater than  $a$ . We assume that this is the case. In the quasisteady case, when we can ignore the compressibility of the fluids and inertial effects, the problem of determining the flow structure near an arbitrary drop can be formulated as follows:

$$\begin{aligned} -\nabla p^+ + \eta_0 \Delta v^+ &= 0, \quad \text{div } v^+ = 0, \quad r \geq a; \\ -\nabla p^* + \eta_1 \Delta v^* &= 0, \quad \text{div } v^* = 0, \quad r \leq a; \\ v_r^+ &= 0, \quad v_r^* = 0, \quad v_t^+ = v_t^*, \quad \sigma_t^+ + \text{grad}_s \tau = \sigma_t^*, \quad r = a; \\ v^*, p^* &< \infty, \quad v^+ \rightarrow e r, \quad r \rightarrow \infty; \\ \sigma^+ &= -p^+ I + 2\eta_0 e^+; \quad \sigma^* = -p^* I + 2\eta_1 e^*. \end{aligned} \quad (3)$$

It will henceforth be convenient to rewrite the expression for the capillary shear stress as follows:

$$\text{grad}_s \tau = \frac{\partial \tau}{\partial \Gamma} \text{grad}_s \Gamma. \quad (4)$$

It follows from (4) that problem (3) can be solved and, thus, the relations (1) and (2) are valid if we know the distribution of the surface concentration  $\Gamma$  of surfactants on the drop and the dependence of the surface tension  $\tau$  on  $\Gamma$ .

As is known from thermodynamics (see [3-5], for example), for equilibrium situations the relation  $\tau(\Gamma^\circ)$  is given by the equation

$$\frac{\partial \tau}{\partial \Gamma^\circ} = -RT \frac{\Gamma^\circ}{C^\circ} \frac{\partial C^\circ}{\partial \Gamma^\circ}, \quad (5)$$

where  $R$  and  $T$  are the universal gas constant and the absolute temperature. The form of the derivative  $\partial C^\circ / \partial \Gamma^\circ$  is determined by the specific adsorption law. For the sake of definiteness, we assume that the surfactant molecules are adsorbed in accordance with the linear Langmuir law. In this case, ignoring surface diffusion of the surfactant, we can write the problem of determining  $\Gamma$  in the form:

$$\begin{aligned} \frac{\partial C}{\partial t} + v^+ \nabla C &= D \Delta C, \quad r \geq a; \quad -D \frac{\partial C}{\partial r} + \alpha(1 - s\Gamma)C - \beta\Gamma = 0; \\ \frac{\partial \Gamma}{\partial t} &= \alpha(1 - s\Gamma)C - \beta\Gamma - \text{div}_s \Gamma v_t^+, \quad r = a; \quad C \rightarrow C^\circ, \quad r \rightarrow \infty. \end{aligned} \quad (6)$$

The first boundary condition of (6) reflects the balance between the adsorbing molecules of surfactant and the desorbing and diffusing (to the drop) solution molecules. The second condition presumes that the surface density of the surfactant may change as a result of sorption-desorption and convective surface flow  $\text{div}_s \Gamma v_t^+$  [3]. It should be noted that the authors of [1] incorrectly formulated the boundary conditions of the problem that are analogous to (6). Thus, the final results obtained in [6] are erroneous. However, the qualitative conclusions in [1] have been confirmed by subsequent analysis.

Problem (3-6) is essentially nonlinear. At present, it cannot be solved analytically in general form. Thus, as in [1], we will restrict ourselves to studying the cases of very large and very small Brenner numbers  $\text{Br} = \|e\| a^2 / D$ , where  $\|e\|$  is the norm of the tensor  $e$ .

Small Values of the Brenner Number ( $\text{Br} \ll 1$ ). Linearizing (4-6) with respect to  $\text{Br}$ , we write

$$C = C^\circ + c, \quad \Gamma = \Gamma^\circ + \gamma, \quad \Gamma^\circ = \frac{\alpha C^\circ}{\alpha s C^\circ + \beta},$$

$$\text{grad}_s \tau = \frac{\partial \tau}{\partial \Gamma^\circ} \text{grad}_s \gamma, \quad \left\{ \frac{c}{C^\circ}, \frac{\gamma}{\Gamma^\circ} \right\} \sim \text{Br}. \quad (7)$$

To solve (3) and calculate the integrals in (2), it is convenient to assume that the tensor  $e$  is given in the form

$$e_{xx} = ex, \quad e_{yy} = -ey, \quad e = \text{const}, \quad (8)$$

while all of the remaining components  $e_{ij}$  are equal to zero. It should be noted that the selection of  $e$  in the form (8) cannot affect the final results, since the sought quantity  $\eta$  is a scalar. However, this choice does make the calculations considerably easier.

Problem (3-6) will be solved in a spherical coordinate system with its origin at the center of the drop. We first apply the Fourier transform to (3-6), which leads to the replacement of the operator  $\partial/\partial t$  by the factor  $i\omega$ .

Retaining the notation for the originals of the quantities as their Fourier components, we obtain the solutions of (3-6) in the form

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

$$c = Gh(r) Y_r, \quad h(r) = r^{-1/2} H_{5/2}(ixr), \quad \kappa = \sqrt{i \frac{\omega}{D}},$$

$$Y_r = \sin^2 \theta \cos 2\varphi, \quad Y_\theta = \sin \theta \cos \theta \cos 2\varphi, \quad Y_\varphi = \sin \theta \sin 2\varphi,$$

where the polar axis is chosen to lie along the  $z$  direction;  $\theta$  and  $\varphi$  are polar and azimuthal angles;  $H_{5/2}$  is the first Hankel function;  $A_j$  and  $G$  are constants of integration whose values are determined from the boundary conditions of linearized variants (3-6).

Having determined the constants  $A_j$  and  $G$ , we find the cartesian components  $v^+$  and  $\sigma^+$ . Using the latter in the integrals (2), we arrive at the following representation for the Fourier components of the operator  $\eta$ :

$$\eta = \eta_0 \left[ 1 + \frac{\eta_0 + 2,5(\eta_1 + B)}{\eta_0 + \eta_1 + B} \rho \right], \quad (10)$$

where

$$B = -\frac{\frac{9}{5} \Gamma^\circ \frac{\partial \tau}{\partial \Gamma^\circ}}{n \frac{Dh'}{mh - Dh'} - i\omega}, \quad h = h(a); \quad h' = \frac{\partial h}{\partial a},$$

$$m = \alpha(1 - s\Gamma^\circ), \quad n = \alpha C^\circ s + \beta, \quad (11)$$

while the derivative  $\partial \tau^\circ / \partial \Gamma^\circ$  is determined from (5) and (7).

Inserting (10) into (1) and using standard representations for Hankel functions [6], after some simple but cumbersome transformations we arrive at the relation

$$P_1 \sigma = 2\eta^\circ P_2 e, \quad (12)$$

where  $P_1$  and  $P_2$  are fifth-degree polynomials in  $(i\omega)^{1/2}$ . The parameter  $\eta^\circ$  is determined as follows:

$$\eta^\circ = \eta_0 \left[ 1 + \frac{\eta_0 + 2,5(\eta_1 + B^\circ)}{\eta_0 + \eta_1 + B^\circ} \rho \right], \quad B^\circ = -\frac{9}{10} \frac{\partial \tau}{\partial \Gamma^\circ} \frac{\Gamma^\circ (ma + 2D)}{Dan}. \quad (13)$$

The physical meaning of  $\eta^\circ$  is the effective viscosity of the emulsion under steady-state conditions ( $\omega = 0$ ). If adsorption is absent ( $B^\circ = 0$ ), then the expression for  $\eta^\circ$  coincides with the classical Taylor formula. With an increase in the influence of adsorptive-capillary phenomena ( $B^\circ/\eta_0 \rightarrow \infty$ ), (13) becomes the Einstein formula for suspensions of hard spheres. The physical reason for such "hardening" of the drops was examined in detail in [1].

The explicit expressions for  $P_1$  and  $P_2$  are not presented here due to their awkwardness. Applying the inverse Fourier transform to (13), after performing the appropriate calculations we arrive at the following rheological equation of state of the emulsion:

$$\left( 1 + \tau_1^{1/2} \int_{-\infty}^t \frac{\partial}{\partial s} \frac{ds}{\sqrt{t-s}} + \tau_2 \frac{\partial}{\partial t} + \tau_3^{3/2} \int_{-\infty}^t \frac{\partial^2}{\partial s^2} \frac{ds}{\sqrt{t-s}} + \right. \\ \left. + \tau_4^2 \frac{\partial^2}{\partial t^2} + \tau_5^{5/2} \int_{-\infty}^t \frac{\partial^3}{\partial s^3} \frac{ds}{\sqrt{t-s}} \right) \sigma = 2\eta^\circ \left( 1 + T_1^{1/2} \int_{-\infty}^t \frac{\partial}{\partial s} \frac{ds}{\sqrt{t-s}} + \right. \\ \left. + T_2 \frac{\partial}{\partial t} + T_3^{3/2} \int_{-\infty}^t \frac{\partial^2}{\partial s^2} \frac{ds}{\sqrt{t-s}} + T_4^2 \frac{\partial^2}{\partial t^2} + T_5^{5/2} \int_{-\infty}^t \frac{\partial^3}{\partial s^3} \frac{ds}{\sqrt{t-s}} \right) e. \quad (14)$$

The characteristic times  $\tau_j$  and  $T_j$  are as follows:

$$\tau_1^{1/2} = \sqrt{\frac{a^2}{\pi D}}, \quad \tau_2 = \frac{a^2}{D} \left[ \mu(\eta_0 + \eta_1) \frac{D}{a^2} + \frac{9}{5} \nu \Gamma' + 4Dn(\eta_0 + \eta_1) \right] f_1, \\ \tau_3^{3/2} = \left( \frac{a^2}{D} \right)^{3/2} \sqrt{\frac{1}{\pi}} \left[ (\eta_0 + \eta_1) \left( n + \frac{\mu}{a^2} \right) + \frac{9}{5} \Gamma' \right] Df_1, \\ \tau_4^2 = \frac{a^2}{D} (\eta_0 + \eta_1) \nu f_1, \quad \tau_5^{5/2} = \frac{9}{5} \left( \frac{a^2}{D} \right)^{3/2} \sqrt{\frac{1}{\pi}} \Gamma' Df_1, \\ T_1^{1/2} = \sqrt{\frac{a^2}{\pi D}}, \quad T_2 = \frac{a^2}{D} \left[ 4\xi Dn + \frac{9}{5} \left( 1 + \frac{5}{2} \rho \right) \Gamma' \nu \right] f_2, \\ T_3^{3/2} = \left( \frac{a^2}{D} \right)^{3/2} \sqrt{\frac{1}{\pi}} \left[ \xi \left( n + \frac{\mu}{a^2} \right) + \frac{9}{5} \left( 1 + \frac{5}{2} \rho \right) \Gamma' \right] Df_2, \quad (15)$$

$$T_4^2 = \frac{a^2}{D} v \xi f_2, \quad T_5^{5/2} = \left( \frac{a^2}{D} \right)^{3/2} \sqrt{\frac{1}{\pi}} \xi D,$$

$$f_1 = \left[ 6(\eta_0 + \eta_1) D n + \frac{9}{5} \mu \right]^{-1}, \quad f_2 = \left[ 6 \xi D n + \frac{9}{5} \left( 1 + \frac{5}{2} \rho \right) \Gamma' \mu \right]^{-1},$$

$$\xi = \eta_0 + \eta_1 + \rho \left( \eta_0 + \frac{5}{2} \eta_1 \right), \quad \mu = 6D + 3\mu a,$$

$$v = 4D + ma, \quad \Gamma' = -\frac{\Gamma^\circ}{a} \frac{\partial \tau}{\partial \Gamma^\circ}.$$

It is evident from (15) that  $\tau_j$  and  $T_j$  are combinations of the time of diffusion relaxation  $\tau_D = a^2/D$  and sorption-desorption  $\tau_S = n^{-1}$ , as well as the time  $\tau_{SD} = (ma/D + ma)\tau_S$ . The time  $\tau_D$  was evaluated in [1], where it was shown that  $\tau_D \sim 10^{-2}$  sec for actual emulsions with micron-size drops, while  $\tau_D \sim 10^4$  sec for emulsions with millimeter-size drops. The times  $\tau_S$  and  $\tau_{SD}$  also fluctuate broadly. While  $\tau_S$  in physical adsorption is small enough so that its effect will not be manifest in actual flows, in chemisorption  $\tau_S$  may be on the order of minutes or even hours. This will lead to significant relaxation phenomena in the case of slow flows of finely dispersed emulsions. For such flows, the diffusion times  $\tau_D$  are too small to affect the character of flow of the mixture.

Large Values of the Brenner Number ( $Br \gg 1$ ). In this case, (6) does not admit linearization with respect to time. To obtain the simplest estimates, as in [1] we use the model of a diffusion boundary layer. In accordance with this model, a drop is assumed to be surrounded by a concentric layer of thickness  $\delta$  ( $\delta \ll a$ ). Meanwhile, outside this layer ( $r > a + \delta$ ), we can ignore the diffusion term in Eq. (6). Inside the layer ( $a < r < a + \delta$ ), the velocity is assumed to be small and we can use it to linearize the problem. The thickness of the boundary layer  $\delta$  can be evaluated by a method similar to that used in [3]:

$$\delta \sim \left( \frac{D}{\|e\|} \right)^{1/2}, \quad \eta_1 \ll \eta_0, \quad \delta \sim \left( \frac{Da}{\|e\|} \right)^{1/3}, \quad \eta_1 \gg \eta_0. \quad (16)$$

In the general case  $\delta \sim \|e\|^{-\ell}$ , where  $1/3 \leq \ell \leq 1/2$ .

Within the framework of the chosen model, the solutions of (6) are represented in the form

$$C = C^\circ, \quad r > a + \delta; \quad C = C^\circ + c, \quad a < r < a + \delta;$$

$$\Gamma = \Gamma^\circ + \gamma; \quad \left\{ \frac{c}{C^\circ}, \frac{\gamma}{\Gamma^\circ} \right\} \sim \frac{v_i^+(a)a}{D}. \quad (17)$$

The quantity  $\gamma$  will be determined directly from the linearized boundary conditions (6), considering that, by virtue of  $\delta \ll a$ ,  $\partial c / \partial r \approx -c / \delta$ . As a result, we arrive at the equation

$$\frac{d\gamma}{dt} = -\psi\gamma - f, \quad \psi = -D \frac{n}{D + m\delta}, \quad f = 3\Gamma^\circ \left( ea - \frac{2}{3} A_{-4} a^{-4} \right) Y_r, \quad (18)$$

which cannot be analyzed by means of linear integral transforms, since the value of  $\delta$  depends on  $e$  and, thus, on time.

We use (3), (4), and (7) to calculate the parameters  $A_{-2}$  and  $A_{-4}$  as functions of  $e$  and  $\gamma$ . Then solving (18) in quadratures, using the results in (1) and (2), and considering the macroscopic isotropy of the emulsion, after calculations we obtain

$$\sigma = 2\eta_0 \left[ e + \left( \frac{2,5\eta_1 + \eta_0}{\eta_1 + \eta_0} e - \frac{3}{10} \frac{\partial \tau / \partial \Gamma^\circ}{\eta_0 + \eta_1} \gamma \right) \rho \right], \quad (19)$$

$$\gamma = \kappa^{-1} \left[ 3\Gamma^\circ a \int \frac{\eta_0 e + \frac{1}{3} \frac{\partial \tau}{\partial \Gamma^\circ} \eta_1 \gamma}{\eta_0 + \eta_1} \kappa dt + \gamma^\circ \right], \quad \kappa = \exp \left( \int \psi dt \right),$$

where  $\gamma^\circ$  is determined from the initial conditions of the problem. Inserting (16) into (19),

we arrive at the conclusion that at  $Br \gg 1$  the relationship between  $\sigma$  and  $e$  is nonlinear and is nonlocal in character with respect to time - the flow pattern of the emulsion depends considerably on the history of the process.

The relationship between  $\sigma$  and  $e$  is simplified considerably in the steady-state case. Calculations show that in this case

$$\sigma = 2\eta^{\circ}e, \quad \eta^{\circ} = \eta_0 \left[ 1 + \frac{\eta_0 + 2.5(\eta_1 + F)}{\eta_0 + \eta_1 + F} \rho \right], \quad (20)$$

$$F = -\frac{9}{10} \frac{\partial\tau}{\partial\Gamma^{\circ}} \frac{\Gamma^{\circ}}{a} \frac{m\delta + D}{Dn}.$$

Comparing (20) and (13), we see that, by virtue of  $\delta \ll a$ ,  $\partial\tau/\partial\Gamma^{\circ} < 0$ , the effective viscosity of the emulsion is less at  $Br \gg 1$  than at  $Br \ll 1$  and approaches its minimum value at  $Br \rightarrow \infty$ .

In conclusion, we noted that the above features of emulsions in surfactant solutions should be manifest to an even greater degree with an increase in the concentration of the disperse phase. Here, new relaxational and nonlinear effects due to the interaction of drops will be seen.

#### NOTATION

$a$ , drop radius;  $C$  and  $C^{\circ}$ , concentration of surfactant near a drop and averaged over the medium;  $c = C - C^{\circ}$ ;  $D$ , diffusion coefficient of the surfactant;  $I$ , second-rank unit tensor;  $n_j$ , components of the unit normal vector to the drop surface;  $r$ , radius vector directed from the center of the drop;  $s$ , surface area of the drop occupied by one molecule of surfactant;  $T_j$  and  $T'$ , characteristic times;  $\alpha$  and  $\beta$ , sorption and desorption constants;  $\Gamma$  and  $\Gamma^{\circ}$ , true and equilibrium surface concentrations of surfactant;  $\eta$ ,  $\eta_0$ , and  $\eta_1$ , effective viscosity and the viscosities of the disperse phase and dispersion medium;  $\rho$ , volume concentration of the disperse phase;  $\tau$ , surface tension of the drop;  $\tau_j$ , and  $\tau'$ , characteristic times. The indices + and \* denote quantities near and inside the drop;  $t$  denotes tangential components of vectors and tensors. The operators  $\text{div}_s$  and  $\text{grad}_s$  have the same meaning as the ordinary divergence and gradient operators, but with fixed values of the radius vector  $r \equiv a$ .

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