CONCENTRATION-CAPILLARY DRIFTING OF DROPLETS IN A CONCENTRATION-STRATIFIED LIQUID SURFACE-ACTIVE AGENT

Yu. K. Bratukhin

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The small parameter method is applied to solve the problem relating to the motion of an insoluble droplet contained within a liquid surface-active agent that is nonuniform with regard to concentration.

The need to study the motion of droplets in liquids arrises in the solution of a number of urgent problems in science and engineering (the breakdown of emulsions [1], various applications of the Stokes–Ribchinskii problem [2], the dissolving of droplets [3], etc.).

Let us determine the velocity and shape of an individual droplet contained within an unbounded concentration-stratified liquid surface-active agent (SAA). Under these conditions, because of the dependence of surface tension on the SAA concentration tangential stresses are developed at the droplet surface, and these lead to interphase convection within the system. We will evaluate these effects under the following assumptions. Both of these liquids are incompressible. All of the parameters of the liquids (density ρ_i, kinematic ν_i and dynamic η_i coefficients of viscosity, coefficients of diffusion D_i in the first (i = 1, unbounded liquid) and in the second (i = 2, droplet) liquids, as well as the surface dilatational η_d and shearing η_s coefficients of viscosity and the coefficient of surface diffusion D_s are constant, with the exception of the coefficient of surface tension σ, which depends linearly on the surface concentration Γ [3] : $\sigma(\Gamma) = \sigma_0(\Gamma_0) + \sigma'(\Gamma - \Gamma_0)$, σ' is a constant. The shape of the droplet $r = R(\theta)$ deviates only slightly from a sphere of radius a : $R = a + \varepsilon(\theta)$, where $|\varepsilon| \ll a$ r, θ, φ represent the coordinates of a spherical system of coordinates whose origin is situated at the center of mass of the dripping droplet, while the polar z axis is directed along the constant gradiant of SAA concentration $\nabla c_\infty = \mathbf{A}$ specified at infinity. The problem is axial symmetrical ($\partial/\partial\varphi = 0$). The motion is slow and creeping. The drip velocity view of the droplet is constant. There is no force of gravity. The liquids are insoluble in each other, whereas the SAA are easily soluble in either of the liquids. The surface of the droplet is easily penetrated by the SAA.

Under these assumptions, the distribution of the velocities $\mathbf{v}_i$, pressures p_i, and concentrations c_i (i = 1, 2) in the liquids is governed by the Navier–Stokes equations of continuity and diffusion [2, 4]:

$$AB(\mathbf{v}_1\nabla)\mathbf{v}_1 = \Delta\mathbf{v}_1 - \nabla p_1;\ ABS(u + \mathbf{v}_1\nabla c_1) = \Delta c_1;\ \nabla\mathbf{v}_i = 0;$$
$$AB\rho(\mathbf{v}_2\nabla)\mathbf{v}_2 = \eta\Delta\mathbf{v}_2 - \nabla p_2;\ ABS(u + \mathbf{v}_2\nabla c_2) = D\Delta c_2. \quad (1)$$

The concentration here is counted from the unperturbed concentration of the point z = ut, at which is located the center of droplet mass at the instant of time t. The equations have been written in dimensionless form. The following have been chosen as the units of length, velocity, pressure, volumetric and surface concentration, i.e., a , $\sigma' A a^2/\eta_1$, $\sigma' A a$, $A a$, $A a^2$. From the dimensionless parameters of the problem

$$A = \frac{Aa}{\rho_1},\ B = \frac{\sigma' a^2}{\nu_1^2},\ \rho = \frac{\rho_2}{\rho_1},\ \eta = \frac{\eta_2}{\eta_1},\ S = \frac{\nu_1}{D_1},\ D = \frac{D_2}{D_1},$$
$$D_s = \frac{D_s}{D_1},\ \delta = \frac{\delta}{a},\ \eta_s = \frac{\eta_s}{a\eta_1},\ \eta_d = \frac{\eta_d}{a\eta_1},\ \sigma = \frac{\sigma_0 a}{\nu_1\rho_1}$$

A is the only one that is monitored during the course of the experiment. The remaining parameters, including the "force" parameter B, which results in the appearance of tangential

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stresses at the boundary of separation, characterized the physical properties of the medium. For the sake of convenience, the dimensional and corresponding dimensionless quantities are identified by the same letters.

Let us formulate the boundary conditions. We will assume for the sake of determinacy that a droplet drips in the direction of the concentration gradient at velocity u (u is the parameter which has to be determined). This is equivalent to the problem, in our reckoning system, to the establishment of the impinging flow at infinity:

$$r \to \infty,\ \mathbf{v}_1 = -u\mathbf{k};\ c_1 = z;\ p_1 = 0. \tag{2}$$

Here we also have written out the conditions for concentration and pressure at infinity, with $\mathbf{k}$ representing the unit vector of the polar axis $z = r\cos\theta$.

At the surface of the droplet $r = R(\theta)$ the normal components of of velocity $\mathbf{n}\mathbf{v}_i = 0$ ($i = 1, 2$) must disappear and the tangential stresses must be continuous: $\boldsymbol{\tau}(\mathbf{v}_1 - \mathbf{v}_2) = 0$. The unit vectors of the normal to the surface $\mathbf{n}$ and tangential to the meridional direction to the surface of the droplet $r = R$ $\boldsymbol{\tau}$ are expressed in terms of the unit vectors of the spherical system of coordinates $\mathbf{e}_r$ and $\mathbf{e}_\theta$ in accordance with formulas

$$\mathbf{n} = (R\mathbf{e}_r - R'\mathbf{e}_\theta)\xi;\ \boldsymbol{\tau} = (R'\mathbf{e}_r + R\mathbf{e}_\theta)\xi;\ \xi = (R^2 + R'^2)^{-1/2}. \tag{3}$$

Under the conditions of the diffusion kinetics of the process [3] between the concentrations within the media, we find that the following relationship is established [3, 5] : $c_1 = Kc_2$, $\Gamma = \delta c_1$. The distribution factor K determines the jump in concentration on transition through the boundary, with the thickness δ of the layer characterizing the distance through which the action of the molecular adsorption forces is propagated.

The balance equation for the mass of the SAA, adsorbed at the surface $r = R(\theta)$, under the conditions of diffusion kinetics, assumes the form [3, 5]

$$ABS\nabla_s(\mathbf{v}^{(s)}\Gamma) = (\nabla c_1 - D\nabla c_2)\mathbf{n} + D_s\Delta_s\Gamma. \tag{4}$$

The subscript s here and beyond denotes the operators and functions pertaining to the surface phase.

In writing the stress continuity conditions at the media separation boundary, we take into consideration the surface effect of viscosity [3, 5], in addition to the volumetric viscous stress tensor $\sigma_{ik}' = \eta(\partial v_i/\partial x_k + \partial v_k/\partial x_i)$, we also introduce the tensor of surface viscous stresses $\sigma_{ik}^{(s)} = \eta_s(\partial v_i^{(s)}/\partial x_k + \partial v_k^{(s)}/\partial x_i - \delta_{ik}\partial v_\ell^{(s)}/\partial x_\ell) + \eta_d\delta_{ik}\partial v_\ell^{(s)}/\partial x_\ell$, in which the possibility of the appearance phase, both of shearing and dilatational stresses, is represented by the coefficients η_s and η_d, respectively. The surface divergence $\nabla_k^{(s)} \times \sigma_{ik}^{(s)}$ is equal to the i-th component of the force f_i, acting on a unit surface in the i-th direction. As a result, the requirement for stress continuity at the media separation boundary $r = R(\theta)$ assumes the form [2, 5]

$$A^2B\Gamma(\mathbf{v}^{(s)}\nabla_s)\,v_i^{(s)} = (p_2 - p_1 + 2H\sigma)\,n_i + (\sigma_{ik}'^{(1)} - \sigma_{ik}'^{(2)})\,n_k + f_i + \nabla_i\sigma. \tag{5}$$

Here 2H represents the average curvature of the surface $r = R(\theta)$ [6]:

$$-2H = \left[(2R^2 + 3R'^2 - RR'') - \operatorname{ctg}\theta\,\frac{R'}{R}\,(R^2 + R'^2)\right]\xi^3. \tag{6}$$

We will solve the formulated problem by the method of perturbations, expanding the solution into series over powers of the parameter A which we will assume to be small: $A \ll 1$. Since the SAA concentration gradient at infinity is contained among the measurement units, the series must be of the Laurent form

$$\psi = \frac{1}{A}\psi^{(-1)} + \psi^{(0)} + A\psi^{(1)} + A^2\psi^{(2)} + \ldots, \tag{7}$$

where $A^n\psi^{(n)}$ is the n-th order of any of these sort functions: velocity, concentration, etc. For example, the shape of the surface $r = R(\theta)$ in accordance with (7) must be written in the form of $r = 1 + A\varepsilon^{(1)} + A^2\varepsilon^{(2)} + \ldots$ elipsis. The calculation is different from zero only for p_2 (Gibbs pressure $p_2^{(-1)} = 2\sigma/B$). For the remaining functions we obtain Taylor series. Thus, the approaching velocity is $u = U + Au^{(1)} + \ldots$.

The functions of zero-th order with respect to A satisfy the following system of equations:

$$\nabla p_1^{(0)} = \Delta \mathbf{v}_1^{(0)};\ \nabla p_2^{(0)} = \eta\Delta \mathbf{v}_2^{(0)};\ \nabla \mathbf{v}_i^{(0)} = 0;\ \Delta c_i^{(0)} = 0,\ (i = 1,\ 2);$$

$$r \to \infty,\ \mathbf{v}_1^{(0)} = -U\mathbf{k},\ c_1^{(0)} = z,\ p_1^{(0)} = 0;$$

$$r = 1,\ v_{r1}^{(0)} = v_{r2}^{(0)} = 0,\ v_{\theta 1}^{(0)} = v_{\theta 2}^{(0)},\ c_1^{(0)} = Kc_2^{(0)},\ \Gamma^{(0)} = \delta c_1^{(0)},$$

$$p_2^{(0)} - p_1^{(0)} - 2\Gamma^{(0)} + 2\frac{\partial v_{r1}^{(0)}}{\partial r} - 2\eta\frac{\partial v_{r2}^{(0)}}{\partial r} + f_r^{(0)} + L\varepsilon^{(1)} = 0,$$

$$\left(\frac{\partial v_{\theta 1}^{(0)}}{\partial r} - v_{\theta 1}^{(0)}\right) - \eta\left(\frac{\partial v_{\theta 2}^{(0)}}{\partial r} - v_{\theta 2}^{(0)}\right) + \frac{\partial \Gamma^{(0)}}{\partial \theta} + f_\theta^{(0)} = 0,$$

$$\frac{\partial c_1^{(0)}}{\partial r} - D\frac{\partial c_2^{(0)}}{\partial r} + D_s\Delta_s\Gamma^{(0)} = 0,\ L = \frac{d^2}{d\theta^2} + \operatorname{ctg}\theta\frac{d}{d\theta} + 2. \quad (8)$$

The exact solution of problem (8) is as follows ($P_1 = \cos\theta$):

$$\mathbf{v}_1^{(0)} = U\left[\left(\frac{1}{r^3} - 1\right)P_1\mathbf{e}_r - \left(\frac{1}{2r^3} + 1\right)r\nabla P_1\right];$$

$$\mathbf{v}_2^{(0)} = -\frac{3}{2}U[(r^2 - 1)P_1\mathbf{e}_r - (1 - 2r^2)r\nabla P_1];$$

$$c_1^{(0)} = \left(r + \frac{\alpha}{r^2}\right)P_1;\ c_2^{(0)} = \frac{1+\alpha}{K}rP_1;\ \Gamma^{(0)} = \delta(1+\alpha)P_1;$$

$$\alpha = \left(1 - \frac{D}{K} - 2D_s\delta\right)\left(2 + \frac{D}{K} + 2D_s\delta\right)^{-1};\ \varepsilon^{(1)} = 0, \quad (9)$$

$$U = -2\delta\left(2 + \frac{D}{K} + 2D_s\delta\right)^{-1}(2 + 3\eta + 2\eta_d)^{-1}. \quad (10)$$

For first-approximation function with respect to A, we derive the following system of equations:

$$-\nabla p_1^{(1)} + \Delta\mathbf{v}_1^{(1)} = B(\mathbf{v}_1^{(0)}\nabla)\mathbf{v}_1^{(0)};\ \Delta c_1^{(1)} = BS(U + \mathbf{v}_1^{(0)}\nabla c_1^{(0)});\ \nabla\mathbf{v}_i^{(1)} = 0;$$

$$-\nabla p_2^{(1)} + \eta\Delta\mathbf{v}_2^{(1)} = B\rho(\mathbf{v}_2^{(0)}\nabla)\mathbf{v}_2^{(0)};\ D\Delta c_2^{(1)} = BS(U + \mathbf{v}_2^{(0)}\nabla c_2^{(0)});$$

$$r \to \infty,\ \mathbf{v}_1^{(1)} = -u^{(1)}\mathbf{k};\ c_1^{(1)} = 0;\ p_1^{(1)} = 0;$$

$$r = 1,\ v_{r1}^{(1)} = v_{r2}^{(1)} = 0;\ v_{\theta 1}^{(1)} = v_{\theta 2}^{(1)};\ c_1^{(1)} = Kc_2^{(1)};\ \Gamma^{(1)} = \delta c_1^{(1)};$$

$$p_2^{(1)} - p_1^{(1)} + 2\frac{\partial v_{r1}^{(1)}}{\partial r} - 2\eta\frac{\partial v_{r2}^{(1)}}{\partial r} + \frac{\sigma}{B}L\varepsilon^{(2)} - 2\Gamma^{(1)} + f_r^{(1)} = 0;$$

$$\left(\frac{\partial v_{\theta 1}^{(1)}}{\partial r} - v_{\theta 1}^{(1)}\right) - \eta\left(\frac{\partial v_{\theta 2}^{(1)}}{\partial r} - v_{\theta 2}^{(1)}\right) + \frac{\partial\Gamma^{(1)}}{\partial\theta} + f_\theta^{(1)} = 0;$$

$$\frac{\partial c_1^{(1)}}{\partial r} - D\frac{\partial c_2^{(1)}}{\partial r} + D_s\Delta_s\Gamma^{(1)} = 0, \quad (11)$$

whose exact solution has the form [$P_2 = 1/2(3\cos^2\theta - 1)$]:

$$\frac{\mathbf{v}_i^{(1)}}{B} = F_iP_2\mathbf{e}_r + G_ir\nabla P_2;\ \frac{c_i^{(1)}}{B} = V_i + W_iP_2;\ \frac{\Gamma^{(1)}}{B} = \gamma_0 + \gamma_2P_2;$$

$$\frac{\varepsilon^{(2)}}{B} = s^{(2)}P_2;\ F_1 = 6C_1\left(\frac{1}{r^2} - \frac{1}{r^4}\right);\ G_1 = \frac{2C_1}{r^4};\ F_2 = 6C_1(r^3 - r);$$

$$G_2 = C_1(5r^3 - 3r);\ V_1 = S\left(\frac{C_2}{r} - \frac{U\alpha}{12r^2}\right);$$

$$W_1 = S\left[\frac{C_3}{r^3} - \frac{U}{6}\left(\frac{1+2\alpha}{r} - \frac{\alpha}{r^4}\right)\right];$$

$$V_2 = \frac{S}{D}\left[\frac{U}{6}\left(\frac{3}{2}\frac{1+\alpha}{K} + 1\right)r^2 + C_4 - \frac{U(1+\alpha)}{8K}\right];$$

$$W_2 = \frac{S}{D}\left(C_5r^2 + \frac{1+\alpha}{14K}Ur^4\right);\ u^{(1)} = 0.$$

The integration constants C_i (i = 1-5), γ_0, γ_2 $s^{(2)}$ are easily found from the boundary conditions of problem (11). In particular, the amplitude $s^{(2)}$, determining the eccentricity of the droplet is as follows:

$$s^{(2)} = \frac{B}{\sigma}\left[\frac{3}{16}U^2(\rho-1) + \delta SU \frac{\frac{1}{3}+\frac{\alpha}{2}+\frac{1+\alpha}{7K}}{3+2\frac{D}{K}+6\delta D_s} \frac{\frac{\eta}{2}+2+2(\eta_s-\eta_d)}{10(1+\eta)+12\eta_s+8\eta_d}\right]. \quad (12)$$

The question of the convergence of expansions (7), such as those used in the solution of problem (1)-(5), is discussed in detail [7].

Let us compare the magnitude of the concentrated [8], electrical [5, 9], and thermal [5, 7, 10] actions on the droplet. For this, we will take into consideration that in the general case the coefficient of surface tension in first approximation depedns linearly on the concentration Γ, the temperature T, and the applied potential difference V : $\sigma = c_0 + \sigma'(\Gamma - \Gamma_0) + \sigma_T(T - T_0) + \sigma_V(V - V_0)$. In view of the linearity of the problem, the total velocity of the droplet will also be equal to the sum of the velocities U, U_T, and U_V, of the stratified [10], nonisothermal, and polarized media, respectively. Since U, U_T, and U_V are respectively proportional to the coefficients σ', σ_T, and σ_V, the relationship between the concentration, thermal, and electrical actions is determined by the relationship between σ', σ_T, and σ_V.

NOTATION

c, concentration; **v**, velocity; p, pressure;, ρ, density; ν, kinematic viscosity; η, dynamic viscosity; D, diffusion factor; Γ, surface concentration; K, distribution factor; δ, layer thickness; r, θ, φ ,coordinates; a , radius of unperturbed droplets; σ, coefficient of surface tension; A, B, S, dimensionless parameters of the problem; P_ℓ, Legendre polynomials of degree ℓ; **n**, **τ** , unit vectors normal and tangential to the droplet surface r = R(θ); $\mathbf{e}_r$, $\mathbf{e}_\theta$, unit vectors of the spherical coordinate system; σ_{ik}, viscous stress tensor; u, drifting velocity; ψ, any of the sort functions; ε, droplet eccentricity; 2H, surface curvature; T, temperature; V, potential difference.

LITERATURE CITED

1. S. S. Voyutskii, A Course in Colloidal Chemistry [in Russian], Moscow (1975).
2. L. D. Landau and E. M. Lifshits, Hydrodynamics [in Russian], Moscow (1986).
3. V. G. Levich, Physicochemical Hydrodynamics [in Russian], Moscow (1959).
4. L. K. Antanovskii and B. K. Konsobynov, Zh. Prikl. Mekh. Tekh. Fiz., No. 2, 59-64 (1986).
5. Yu. A. Buevich and L. M. Rabinovich (eds.), The Hydrodynamics of Interphase Surfaces [in Russian], Moscow (1984).
6. H. Korn and T. Korn, Mathematics Handbook [Russian translation], Moscow (1978).
7. Yu. K. Bratukhin, Inzh.-Fiz. Zh., 32, No. 2, 251-256 (1977).
8. V. G. Levich and A. M. Kuznetsov, Dokl. Akad. Nauk SSSR, 146, No. 1, 1261-1262 (1962).
9. S. S. Dukhin and B. V. Deryagin, Electrophoresis [in Russian], Moscow (1976).
10. V. A. Mankevich, Inzh.-Fiz. Zh., 41, No. 6, 1040-1045 (1981).