Physical Chemistry

Corresponding Member of the USSR Academy of Sciences V. G. Levich, A. M. Kuznetsov

1962

SovietRxiv

Abstract

Full Text

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ON THE MOTION OF DROPS IN LIQUIDS UNDER THE ACTION OF SURFACE-ACTIVE SUBSTANCES

In a number of works, the retardation of the phase-boundary surface produced by surface-active substances has been investigated. If, however, the phase-boundary surface is in a concentration-gradient field, the surface-active substance can cause active motion.

Let us consider a drop of liquid placed in a liquid medium in which there is a maintained concentration gradient of a dissolved surface-active substance. We choose the direction of the gradient as the x-axis. We shall assume that the surface-active substance is insoluble in the liquid of the drop, and that the exchange process between the volume of the solution and the surface of the drop is determined by the rate of supply of the substance to the surface. As a consequence of the fact that the surface-active substance is distributed nonuniformly in the solution, there will be a nonuniform distribution of its concentration on the surface of the drop. Then the surface tension will vary along the surface of the drop, and it must set the drop in motion. We shall find the velocity of this motion, considering it stationary and slow.

The hydrodynamic equations for the liquid outside and inside the drop are

$$\nabla p = \mu \Delta \mathbf{v}, \qquad \operatorname{div} \mathbf{v} = 0, \tag{1}$$

$$\nabla p' = \mu' \Delta \mathbf{v}', \qquad \operatorname{div} \mathbf{v}' = 0, \tag{2}$$

where μ and μ' are the viscosities of the medium and of the drop.

The distribution of the concentration of the surface-active substance is described by the equation

$$(\mathbf{v}\nabla)c = D\Delta c. \tag{3}$$

At the surface of the drop the condition

$$D\frac{\partial c}{\partial n} = \mathrm{div}_S\,\Gamma \cdot \mathbf{v}_t, \tag{4}$$

must be satisfied, where n is the outward normal to the surface of the drop; Γ is the surface concentration; $\mathbf{v}_t$ is the velocity of the liquid at the surface of the drop.

We shall seek an approximate solution of the system of equations of convective diffusion and hydrodynamics, assuming that the change of surface tension along the drop is small (cf. ([1])). Suppose that one may neglect the dependence of the thickness of the diffusion layer on the point on the surface of the drop, replacing it by some mean value δ. Then one may write approximately

$$D\frac{\partial c}{\partial n} \approx D\frac{\Delta c}{\delta}, \tag{5}$$

where Δc is the difference of concentrations between the volume of the solution and a point near the surface of the drop.

We denote by c_1 the value of the concentration at the surface, in equilibrium with Γ. We denote the concentration in the volume by c^*. The concentration distribution in the volume may be represented in the form

$$c^* = (\nabla c)x + c_0. \tag{6}$$

c_0 is the value of the concentration at the point $x = 0$ and at the same time is the mean value of the concentration on the segment from $x = -a$ to $x = a$ (a is the radius of the drop), corresponding to a certain equilibrium concentration Γ_0 on the surface of the drop. Let us pass to the coordinate system in which the drop is at rest.

Since the velocity of the drop is small, one may assume that the difference $\Delta c = c^* - c_1$ will have the same value in the laboratory coordinate system and in the system of the stationary drop,

$$\Delta c = (\nabla c)x' - \frac{\partial c}{\partial \Gamma}\Gamma', \tag{7}$$

where $\Gamma' = \Gamma - \Gamma_0$. It can be shown that this assumption is valid if the inequality $u \ll Dc_0/\delta^2\nabla c$ is satisfied. The velocity on the surface of the drop may be represented in the form $v_0 \sin\theta$, where θ is the polar angle measured from the positive direction of the x axis.

Let us rewrite the boundary condition (4), neglecting terms of second order of smallness and passing to spherical coordinates:

$$\frac{D}{\delta}\left[(\nabla c)(a+\delta)\cos\theta - \frac{\partial c}{\partial \Gamma}\Gamma'\right] = \frac{2v_0\Gamma_0}{a}\cos\theta. \tag{8}$$

Hence

$$\Gamma' = \left[(\nabla c)(a+\delta) - \frac{2v_0\Gamma_0\delta}{Da}\right]\frac{\cos\theta}{\partial c/\partial\Gamma}. \tag{9}$$

The surface tension may be represented in the form

$$\sigma = \sigma_{\pi/2} + \int_{\pi/2}^{\theta}\frac{\partial\sigma}{\partial\theta}\,d\theta = \sigma_{\pi/2} + \int\frac{\partial\sigma}{\partial\Gamma}\frac{\partial\Gamma}{\partial\theta}\,d\theta =$$

$$= \sigma_{\pi/2} + \left[(\nabla c)(a+\delta) - \frac{2v_0\Gamma_0\delta}{Da}\right]\frac{\partial\sigma}{\partial c}\cos\theta. \tag{10}$$

Knowing the distribution of concentration on the surface of the drop, one can solve the hydrodynamic problem.

In the coordinate system moving together with the drop, a flow with velocity $(-u)$ impinges on the drop. Far from the drop the velocity distribution has the form

$$v_r = u\cos\theta, \qquad v_\theta = -u\sin\theta, \qquad r\to\infty. \tag{11}$$

The boundary conditions on the surface of the drop $(r=a)$ will be

$$v_r = v_r' = 0, \qquad v_\theta = v_\theta',$$

$$-p + 2\mu\frac{\partial v_r}{\partial r} = -p' + 2\mu'\frac{\partial v_r'}{\partial r} + p_\sigma, \tag{12}$$

$$\mu\left(\frac{1}{r}\frac{\partial v_r}{\partial\theta} + \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r}\right) = \mu'\left(\frac{1}{r}\frac{\partial v_r'}{\partial\theta} + \frac{\partial v_\theta'}{\partial r} - \frac{v_\theta'}{r}\right) + p_t,$$

where

$$p_\sigma = \frac{2\sigma}{a} = \frac{2\sigma_{\pi/2}}{a} + \frac{2}{a}\left[(\nabla c)(a+\delta) - \frac{2\Gamma_0 v_0\delta}{Da}\right]\frac{\partial\sigma}{\partial c}\cos\theta,$$

$$p_t = -\frac{1}{a}\frac{\partial\sigma}{\partial\theta} = \frac{1}{a}\left[(\nabla c)(a+\delta) - \frac{2\Gamma_0 v_0\delta}{Da}\right]\frac{\partial\sigma}{\partial c}\sin\theta. \tag{13}$$

Solutions of the hydrodynamic equations satisfying the boundary conditions (12)–(13) and the condition of finiteness at the point $r = 0$ in the internal liquid will have the form:

for the external liquid:

$$v_r = \left(\frac{b_1}{r^3} + \frac{b_2}{r} + b_3\right)\cos\theta,$$

$$v_\theta = \left(\frac{b_1}{2r^3} - \frac{b_2}{2r} - b_3\right)\sin\theta,$$

$$p = \mu\frac{b_2}{r^2}\cos\theta + b_0;$$

for the internal liquid:

$$v'_r = (a_1 r^2 + a_2)\cos\theta,$$

$$v'_\theta = -(2a_1 r^2 + a_2)\sin\theta,$$

$$p' = \mu' 10 a_1 r\cos\theta + a_0.$$

Substituting these solutions into the boundary conditions, one can find the constants b_1, b_2, b_3, a_1, a_2.

The calculations lead to the following expression for the velocity of motion of the drop:

$$u = \frac{(\nabla c)(a+\delta)\left|\frac{\partial\sigma}{\partial c}\right|}{2\mu + 3\mu' + \frac{2\Gamma_0\delta}{Da}\left|\frac{\partial\sigma}{\partial c}\right|}.$$

The expression found is similar to the formula for the velocity of motion of a liquid metallic drop in an electric field ([1]), since the mechanism that sets the drop in motion–the change of surface tension along the surface of the drop–is the same in both cases.

An almost identical expression, based on considerations founded on this analogy, was obtained independently of us by A. N. Frumkin ([2]).

Institute of Electrochemistry
Academy of Sciences of the USSR

Received
5 IV 1962

References Cited

[1] V. G. Levich, *Physicochemical Hydrodynamics*, Moscow, 1959.
[2] A. N. Frumkin, S. S. Satyianarayana, N. V. Nikolaeva-Fedorovich, *Izv. AN SSSR, OKhN* (in press).

Note: Figure translations are in progress. See original paper for figures.