DROPLET MOTIONS IN LIQUIDS CAUSED BY SURFACE ACTIVE SUBSTANCES

Corr. Member, AN SSSR, V. G. Levich
and A. M. Kuznetsov

Institute of Electrochemistry, Academy of Sciences, USSR
Translated from Doklady Akademii Nauk SSSR, Vol. 146, No. 1,
pp. 145-147, September, 1962
Original article submitted April 5, 1962

A number of papers have been devoted to a study of the interface hindrance produced by surface-active substances. If, however, the interface is in a field with a concentration gradient, a surface-active substance can produce active motion.

Consider a drop of liquid in a liquid medium in which there is a sustained gradient in the concentration of the dissolved surface-active substance. The direction of the gradient is taken to be the x axis. Let us assume that the surface-active substance is insoluble in the liquid of the drop, while the exchange between the volume of the solution and the surface of the drop is determined by the rate at which material is supplied to the surface. Because of the fact that the surface-active substance is not uniformly distributed in the solution, its concentration will not be uniform over the surface of the drop. Then the surface tension will change over the surface of the drop, and it must start to move. We shall find the rate of the motion, assuming that it is steady state and slow.

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

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

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

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

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

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

On the surface of the drop the condition to be satisfied is

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

where n is the external normal to the drop surface, Γ is the surface concentration, and $\mathbf{v}_t$ is the velocity of the liquid at the drop surface.

We shall look for an approximate solution of the system of convective diffusion and hydrodynamic equations, assuming that the change in surface tension over the drop is small (compare [1]). Assume that we can neglect any changes in diffusion-layer thickness over the surface of the drop, giving it some mean value δ. Then we can write approximately

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

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

The concentration at the surface, in equilibrium with Γ, is denoted by c_1. The concentration in the volume is denoted by c^*. The concentration distribution in the volume may be written in the form

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

The quantity c_0 is the concentration at the point $x = 0$, and at the same time is the mean value of the concentration in the interval from $x = -a$ to $x = a$ (a is the radius of the drop), corresponding with some equilibrium concentration Γ_0 on the surface of the drop. We now pass to a coordinate system in which the drop is at rest.

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

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

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

We write the boundary condition (4) neglecting second-order terms and, passing to spherical coordinates, we obtain

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

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 written 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 concentration distribution on the drop surface, we can solve the hydrodynamic problem.

In the coordinate system moving with the drop, the drop is approached by a stream moving with the velocity $(-u)$. Far from the drop the velocity distribution has the form

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

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

$$v_r = v_r' = 0, \quad v_\theta = v_\theta',$$
$$-p + 2\mu\frac{\partial v_r}{\partial r} = -p' + 2\mu'\frac{\partial v_r'}{\partial r} + p_\sigma, \tag{12}$$
$$\mu\left(\frac{1}{r}\frac{\partial v_r}{\partial\theta} + \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r}\right) = \mu'\left(\frac{1}{r}\frac{\partial v_r'}{\partial\theta} + \frac{\partial v_\theta'}{\partial r} - \frac{v_\theta'}{r}\right) + p_t,$$

where

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

The solutions of the hydrodynamic equations satisfying the boundary conditions (12)-(13) and the finiteness conditions 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 in the boundary conditions, we find the constants b_1, b_2, b_3, a_1, and a_2. The calculations lead to the following expression for the rate 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 rate of motion of a liquid metal drop in an electric field [1], since the mechanism which sets the drop in motion – the variation in surface tension over the drop surface – is the same in both cases.

An almost identical expression using concepts based on this analogy was obtained independently of our work by A. N. Frumkin [2].

LITERATURE CITED

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