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Abstract

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The Diffusion-Electric Potential of a Falling Drop with an Adsorption Layer

The electric field of a particle at rest is localized, as is known, within the limits of the electric double layer. The situation changes, however, if one takes into account the motion of the drop relative to the surrounding medium and the mobility of its surface. The emergence of an electric field during the motion of a liquid interface was first considered by Frumkin and Levich (^1) for the case of a mercury drop falling in an electrolyte solution. In this case it was necessary to take into account the adsorption-desorption process of only one kind of ion—the mercury ions—since the inner lining of the double layer was represented by the free electrons of mercury. It therefore proved possible to take into account only the migration of ions in the electric field, neglecting diffusion. In the present work a qualitatively different process is considered, when two types of ions from an electrolyte solution are adsorbed on the mobile surface of a drop. Preservation of the approximate electroneutrality of the double layer under conditions of its continuous renewal requires approximate equality of the quantities of positive and negative charges arriving from the bulk of the solution. In the absence of an electric field, this condition can be satisfied only when the diffusion coefficients of the ions are equal in magnitude. If, however, the diffusion coefficients are not equal, an electric field arises that equalizes the supply of positive and negative ions to the surface. Phenomena of this kind are analogous to diffusion potentials.

We shall consider the diffusion-electric effect that occurs when a drop of electrolyte solution falls in a liquid or gaseous medium (for example, in oil or in air), which for the sake of simplicity we shall assume to be devoid of ions.

Let Γ^+ and Γ^- be the adsorptions of positive and negative ions, and v_t the velocity of the liquid at the surface of the drop. Motion of the drop surface is accompanied by convective transport of adsorbed positive and negative ions, the densities of the surface fluxes of which are respectively equal to $\Gamma^+ v_t$ and $\Gamma^- v_t$. It is not difficult to see that the surface divergences of these fluxes are different from zero. Meanwhile, under stationary conditions the local surface densities of ions must be preserved. The difference in the arrival and loss of adsorbed ions, occurring owing to the convective surface flux, must be compensated by the corresponding normal component of the volume flux of ions j_n, caused by migration of the ions in the electric field and by their diffusion:

$$\operatorname{div}_s(\Gamma^+ v_t) = j_n^+ = \left(-D^+ \frac{\partial C^+}{\partial r} + \frac{F}{RT} D^+ z^+ C^+ E_{1r}\right)_a, \tag{1}$$

$$\operatorname{div}_s(\Gamma^- v_t) = j_n^- = \left(-D^- \frac{\partial C^-}{\partial r} - \frac{F}{RT} D^- z^- C^- E_{1r}\right)_a, \tag{2}$$

where E_{1r} is the radial component of the electric field at the inner side of the surface, F is Faraday' s number, R the gas constant, T the absolute temperature, and a the radius of the bubble.

The principal factor simplifying the determination of the potential distribution in the electrolyte is the assumption of electroneutrality (^{2}) in its volume:

$$z^+ C^+ - z^- C^- = 0. \tag{3}$$

An analogous condition must also be satisfied for the adsorption:

$$z^+ \Gamma^+ - z^- \Gamma^- = 0. \tag{4}$$

Using (3) and (4), it is convenient to introduce the bulk molar concentration C and the surface molar concentration Γ

$$C = \frac{C^+}{z^-} = \frac{C^-}{z^+}, \qquad \Gamma = \frac{\Gamma^+}{z^-} = \frac{\Gamma^-}{z^+}.$$

Eliminating C^+ and C^- from (1) and (2) with the aid of (3) and accepting condition (4), we obtain:

$$E_{1r}(\theta) = \frac{RT}{F} \frac{D^+ - D^-}{D^+ D^-} \frac{\operatorname{div}_s(\Gamma v_t)}{(z^+ + z^-)C}. \tag{5}$$

To determine the electric potential in the volume of the drop, one should consider the continuity equations for the ion fluxes in the volume of the electrolyte, which, under condition (3), take the form (^{2}),

$$\mathbf{v}\, \operatorname{grad} C = D_{ef} \Delta C \tag{6}$$

$$\frac{F}{RT}(z^+ D^+ + z^- D^-) C \mathbf{E}_1 + (D^+ - D^-) \operatorname{grad} C = \frac{\mathbf{i}}{F z^+ z^-}, \tag{7}$$

where

$$D_{ef} = \frac{D^+ D^- (z^+ + z^-)}{z^+ D^+ + z^- D^-},$$

v is the velocity distribution, and **i** is the density of the total electric current. Thus, to determine the electric field, one must first solve the equation of convective diffusion (6), and then use (7), for which, in addition, knowledge of the distribution of the total current is required.

Using (1), (2), and condition (4), we shall show that the normal component of the current at the surface of the drop is, in the first approximation, equal to zero

$$i_n = (i_n^+ - i_n^-) = z^+ e j_n^+ - z^- e j_n^- = \mathrm{div}_s[(z^+ \Gamma^+ - z^- \Gamma^-) e V_t] = 0. \tag{8}$$

To verify that, in the case under consideration, the density of the total current is zero everywhere, we transform (7) to the form

$$\mathbf{i}(r,\theta) = C(r,\theta)\,\mathrm{grad}\,\Psi(r,\theta), \tag{9}$$

where

$$\Psi(r,\theta) = F z^+ z^- \left[\frac{F}{RT}(z^+ D^+ + z^- D^-) + (D^+ - D^-)\ln C\right],$$

$\varphi(r,\theta)$ is the electric potential. We now express, through Ψ, the continuity equation for the total current $\mathrm{div}\,\mathbf{i} = 0$ and the boundary condition, easily obtained from (8) and (9), if one takes into account that $C(a,\theta) \neq 0$:

$$\mathrm{div}[C(r,\theta)\,\mathrm{grad}\,\Psi(r,\theta)] = 0, \qquad \frac{\partial \Psi}{\partial r}(a,\theta) = 0.$$

It is not difficult to show analytically, or by using, for example, the method of thermal analogy, that this problem has only the trivial solution

$$\Psi(r,\theta) = \mathrm{const},$$

so that

$$\mathbf{i}(r,\theta) = 0. \tag{10}$$

Taking (10) into account, we transform (7) to the form

$$\vec{E}_1 = -\frac{RT}{F}\,\frac{D^+ - D^-}{z^+ D^+ + z^- D^-}\,\mathrm{grad}\ln C, \tag{11}$$

whence there immediately follows the formula relating the potential distribution $a\varphi_1(r, \Theta)$ to the concentration distribution:

$$\varphi_1(r,\theta) = \frac{RT}{F}\frac{D^+ - D^-}{z^+D^+ + z^-D^-}\ln\frac{C}{C_0} + \varphi_0, \tag{12}$$

where C_0 is the concentration at the equator of the drop.

Let us consider the question of the electric field of the drop in the special case of small differences in ion concentration

$$C(r,\theta) - C_0 \ll C_0. \tag{13}$$

Since, according to (13), the volume concentration everywhere at the surface almost coincides with C_0, the deviation of $\Gamma(\theta)$ from Γ_0 must be small*:

$$\Gamma(\theta) - \Gamma_0 \ll \Gamma_0. \tag{14}$$

The distribution of velocities along the surface of the drop for $\mathrm{Re} \ll 1$ has the form (3)

$$v_t = v_0 \sin\theta. \tag{15}$$

Substituting (15) into (5) and taking (14) and (13) into account, we transform (5) to the form

$$E_{1r}(\theta) = -\frac{2RT}{F(z^+ + z^-)}\frac{D^+ - D^-}{D^+D^-}\frac{v_0}{a}\frac{\Gamma_0}{C_0}\cos\theta. \tag{16}$$

Eliminating E_{1r} from (1) and (2), using (3), (4), and (15), with allowance for (14), gives a simple boundary condition for determining $C(r,\theta)$

$$\frac{\partial C}{\partial r}(a,\theta) = 2\frac{v_0\Gamma_0}{D_{ef}a}\cos\theta. \tag{17}$$

Let us formulate a criterion characterizing the conditions of diffusion inside the drop, giving the order of magnitude of the ratio of the convective flux to the diffusive one:

$$\mathrm{Pe} = \frac{av_0}{D_{ef}}\frac{C_0}{\delta C},$$

where the concentration difference in the drop may be estimated as the concentration difference along its surface between the equator and the pole

$$\delta C = C_0 - C(a,0), \quad v_0 = \frac{3}{2} U_0 \frac{\eta_2 + \eta_1 + \gamma}{2\eta_2 + 2\eta_1 + 3\gamma}, \quad U_0 = \frac{2}{9} \frac{a^2 g(\rho_1 - \rho_2)}{\eta_2},$$

where U_0 is the velocity of fall of the drop in the given medium, η_2 and ρ_2 are the viscosity and density of the medium, η_1 and ρ_1 are the viscosity and density of the substance of the drop, and γ is the coefficient of retardation, which we shall neglect. Under the condition

$$\mathrm{Pe} \ll 1 \tag{18}$$

the convective transport of ions may be neglected in comparison with the diffusive transport, which makes it possible in this case to replace (6) by Laplace' s equation

$$\Delta C = 0. \tag{19}$$

Its solution, together with the boundary conditions $C\left(a, \frac{\pi}{2}\right) = C_0$ and (17), presents no difficulty:

$$C(r,\theta) = C_0 \left(1 + \frac{\delta C}{C_0} \frac{r}{a} \cos\theta\right), \tag{20}$$

where, as is seen from (17),

$$\frac{\delta C}{C_0} = 2 \frac{v_0}{D_{ef}} \frac{\Gamma_0}{C_0}, \tag{21}$$

so that condition (13) is replaced in the following way: $2 \frac{v_0}{D_{ef}} \frac{\Gamma_0}{C_0} \ll 1$, or

$$\Gamma_0 / C_0 \ll \tfrac{1}{2} D_{ef} / v_0. \tag{13'}$$

* It is assumed that the deviation from adsorption equilibrium at each point of the surface is small.

Substituting (21) into the dimensionless criterion Pe, we now write condition (18) in the following form

$$\mathrm{Pe} \sim \frac{aC_0}{\Gamma_0} \ll 1. \tag{18'}$$

Conditions $(13')$ and $(18')$ are conveniently combined:

$$a \ll \frac{\Gamma_0}{C_0} \ll \frac{1}{2}\frac{D_{ef}}{v_0}. \tag{22}$$

As numerical calculation shows in the case of a water-aerosol droplet, this condition is well satisfied* for $a \lesssim 1\mu$. For $a \simeq 3\mu$, the results presented above can be used only for estimating the desired value of the electric-field strength for values of Γ_0/C_0 lying within the narrow limits determined from (22).

Substituting (20) into (12) and neglecting terms higher than first order of smallness relative to $\delta C/C_0$, we obtain

$$\varphi_1(r,\theta) = \frac{2RT}{F}\frac{D^+ - D^-}{z^+D^+ + z^-D^-}\frac{v_0}{D_{ef}}\frac{\Gamma_0}{C_0}\frac{r}{a}\cos\theta + \varphi_0. \tag{23}$$

In determining the external electric field of the droplet we shall not take into account the ionization of the air, as a result of which the potential distribution in the air $\varphi_2(r,\theta)$ must satisfy Laplace' s equation

$$\Delta\varphi_2 = 0. \tag{24}$$

The potential jump at the droplet surface δV will be assumed independent of the angle θ, which corresponds to sufficiently small values of adsorption that do not cause a noticeable change in the potential jump**

$$\varphi_2(a,\theta) - \varphi_1(a,\theta) = \delta V. \tag{25}$$

The potential distribution satisfying (24) and (25) has the form

$$\varphi_2(r,\theta) = \frac{2RT}{F}\frac{D^+ - D^-}{z^+D^+ + z^-D^-}\frac{v_0}{D_{ef}}\frac{\Gamma_0}{C_0}\frac{a^2}{r^2}\cos\theta, \tag{26}$$

where $\varphi_0 = -\delta V$ has been adopted, which ensures a zero value of the potential at infinity.

If one takes $a \sim 3\mu$, $\delta C/C_0 \sim 0.3$, the electric-field strength at the droplet surface $E_2(a,\pi) = \operatorname{grad}\varphi_2(a,\pi)$ is 100 V/cm.

In reality, such a large value of the electric-field strength under these specific conditions is not realized because of electrocapillary braking of the surface, which we have not taken into account. Calculation shows that at $E \sim 100$ V/cm the electric field must retard the motion of the surface, so that such an electric field cannot be realized. Conversely, already at 10 V/cm the tangential electric forces retarding the motion of the surface are an order of magnitude smaller than the viscous forces, so that the electrocapillary effect in this case may be neglected.

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2. V. G. Levich, *Physicochemical Hydrodynamics*, § 39, Publishing House of the Academy of Sciences of the USSR, 1952.

3. Ibid., §§ 53–61.

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* The theory presented can without particular difficulty be generalized to the case Pe $\gg$ 1, when the electric field in the droplet proves to be localized in a thin boundary layer. Consideration of this question should be the subject of a separate article.

** The theory presented is readily generalized to the case of high concentrations of the surface-active substance, when the change in the potential jump along the surface and the braking of its motion by the adsorbed substance must be taken into account. This case is not considered here, as being less interesting, since when the surface is braked the electric field decreases.

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

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