

## LITERATURE CITED

1. N. P. Gnusin, N. P. Poddubnyi, and A. I. Maslii, Principles of Theory of Calculating and Simulating Electrical Fields in Electrolytes [in Russian], Nauka, Novosibirsk (1972).
2. I. B. Mohler, Metal Finishing, 46, 59 (1948).
3. N. P. Gnusin and G. N. Zrazhevskii, Zh. Fiz. Khim., 32, 1003 (1958).

## ELECTROPHORETIC FORCE ALONG EQUIPOTENTIAL ELECTRODE

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The conditions under which the electric fields in the bodies of the electrode and the electrolyte are identical in magnitude and direction are examined. A plane solid electrode in a variable field oriented along the interface is subject to an electrophoretic force with an amplitude proportional to the square root from the ratio of the field frequency to the electrolyte viscosity. The leakage of alternating current from the electrolyte to the electrode, generated by the micro-roughness of the interface, is negligible. An approximate expression is derived for the dependence of the electrophoretic force attenuation coefficient on the roughness factor.

Among the great creative heritage left by A. N. Frumkin are papers on electrophoresis. In one of them [1] the influence of the electrode potential on the electrophoretic force perceptible to the electrode is studied for the first time. The electrophoretic force  $f$  is known to fall with a reduction in the thickness of the moving part of the double layer  $\delta$  (an increase in the electrolyte concentration) and with an increase in the length of the solid body  $l$  in accordance with the law  $f \approx -(\delta/l) f_k$ , where  $f_k$  is the coulomb force acting on the charge of the moving part of the double layer. For example, when  $\delta = 10^{-6}$  cm and  $l = 1$  cm we have  $f \approx -10^{-6} f_k$ . A diluted electrolyte (with a high  $\delta$ ) and a thin wire in a transverse electrical field (with a low  $l$ ) are therefore used in experiments [1]. A reduction in the wire diameter also promotes a reduction in the potential drop along the electrode. Such a drop introduces an element of uncertainty to the magnitude of the potential of the electrode relative to the electrolyte.

Investigations into electrophoresis in a variable field have been resumed recently in A. N. Frumkin's laboratory [3]. An approach has been found based on the fact, that an electric field oriented along the electrode/electrolyte interface is generated on both sides of the boundary: not only in the electrolyte but also in the electrode [4]. Thanks to this the potential of the electrode relative to the electrolyte remains identical at all points on the electrode and constant in time regardless of the length of the electrode, the magnitude of the field, and the nature of the change in the field in time.

A field which is sinusoidal in time and tangential to the electrode surface then becomes practicable, which would be impossible under normal conditions due to the leakage of current from the electrolyte to the electrode through the capacity of the double layer. In a variable field the plane electrode is subject to an electrophoretic force, while there is no such force in a constant field.

The moving lining of the double layer carries with it the adjoining electrolyte. In a stationary field the velocities in the electrolyte are equalized. It is displaced as a whole together with the outer part of the lining and does not inhibit the movement. Only the force of the friction between the moving and unmoving linings, which are subject in the field to coulomb forces identical in magnitude but opposed in direction, shows any resistance to movement. Through the friction both forces compensate each other completely. The resultant of the forces perceptible to the surface of the solid is equal to zero - there is no electrophoretic effect.

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In a variable field the displacement of the moving part of the double layer excites shear waves in a layer of electrolyte  $\lambda = \sqrt{2\mu/\omega}$  thick, where  $\omega$  is the angular velocity of the field and  $\mu$  is the kinematic viscosity of the electrolyte. The electrolyte enters into the inhibition of the moving lining. The compensation of the forces between the linings is disrupted. An electrophoretic force is generated which acts on the plane solid electrode and is equal in magnitude to the force of the friction at the boundary between the moving part of the double layer and the electrically neutral body of the electrolyte.

The  $\delta/l$  criterion is replaced by the  $\delta/\lambda$  criterion,  $f = -(\delta/\lambda)f_k$  when  $\lambda \ll l$ . For example in a dilute aqueous solution at a frequency of 1 kHz and at 20°C, we have  $\lambda = 1.8 \cdot 10^{-3}$  cm;  $f = -0.56 \cdot 10^{-3} f_k$  when  $\delta = 10^{-6}$  cm.

The variable electrophoretic force is measured experimentally by comparing its action on the electrode with the action of a known external variable force. Both forces are equal if they give an identical amplitude of the stress in the linings of the piezoelectric element clamped to the electrode [4]. It is also possible to measure the stationary electroosmosis along an equipotential electrode.

Let us calculate the electrophoretic force accurately. Let us orient the x axis perpendicular to the interface surface. Let us select the zero point in the plane, located at a distance of z from the slip plane, which separates the moving part of the double layer from the unmoving part. Let a thin layer of the electrolyte in the  $x=0$  plane carry a charge with a surface density q and be displaced in a tangential electrical field E at a velocity  $v_p$ . The  $x=0$  layer carries with it the fluid lying on either side of it. The velocity of the fluid at a point x at a moment in time, t,  $v(x, t)$ , satisfies the equation

$$\begin{cases} \frac{\partial^2 v}{\partial x^2} - \frac{1}{\mu} \frac{\partial v}{\partial t} = 0, \\ v(z) = 0; \quad v(0) = v_p; \quad v(-\infty) < \infty. \end{cases} \quad (1)$$

Let  $v_p = y_0 \exp i\omega t$ . Let us seek a solution in the form of  $v = y \exp i\omega t$ . Then

$$\begin{cases} \frac{d^2 y}{dx^2} - \frac{i\omega}{\mu} y = 0, \\ y(z) = 0; \quad y(0) = y_0; \quad y(-\infty) < \infty. \end{cases} \quad (2)$$

The solution to the edge problem (2)

$$\begin{cases} y(x) = y_0 [e^{a(2z-x)} - e^{ax}] / (e^{2az} - 1), & 0 < x < z \\ y(x) = y_0 e^{ax}, & -\infty < x < 0, \end{cases} \quad (3)$$

where

$$a = \sqrt{\omega/2\mu} (1+i). \quad (4)$$

In the field  $E = E_0 \cos \omega t$  ( $E = E_0 \exp i\omega t$ ) a coulomb force  $f_k = -qE_0 \exp i\omega t$  acts on the  $x=0$  layer. It is compensated by the friction force

$$f_p = \eta [dy/dx(+0) - dy/dx(-0)] \exp i\omega t, \quad (5)$$

where  $\eta$  is the viscosity. From (5) and the equality  $f_p + f_k = 0$  we find

$$y_0 = -(qE_0/2\eta a) (1 - e^{-2az}). \quad (6)$$

The surface of the solid is subject to a friction force

$$f_s = -\eta dy/dx(x=z) e^{i\omega t} = -qE_0 e^{-az} e^{i\omega t} \quad (7)$$

and a coulomb force  $\bar{f}_k = -f_k = qE_0 \exp i\omega t$ . Their resultant is the electrophoretic force

$$f = f_s + \bar{f}_k = qE_0 (1 - e^{-az}) e^{i\omega t}. \quad (8)$$

Let the charge density  $\rho$  be predetermined as a function of the distance z from the slip plane  $\rho = \rho(z)$ . A layer dz thick makes a contribution to the electrophoretic force governed by Eq. (8) in which  $q = \rho(z) dz$  should be assumed:

$$f = E_0 \int_0^z \rho(z) (1 - e^{-az}) dz e^{i\omega t}. \quad (9)$$

Further, let  $\epsilon$  be the dielectric constant and  $\psi(z)$  be the potential. By using Poisson's equation  $\rho = \epsilon d^2\psi/dz^2$  (SI system) and integrating (9) by parts we arrive at the expression being sought for the electrophoretic force

$$f = \varepsilon E_0 a \left[ \psi(0) - a \int_0^{\infty} \psi(z) e^{-az} dz \right] e^{i\omega t}. \quad (10)$$

Here  $\psi(0) = \zeta$  is the electrokinetic potential.

Virtually always  $|az| \ll 1$ . In the example examined above  $|az| < 0.8 \cdot 10^{-3}$ . With this kind of accuracy the integral in (10) can be neglected. Thus, in cases of practical importance the formula for the variable electrophoretic force on the plane equipotential electrode takes the form

$$f = \varepsilon \zeta E_0 \sqrt{\frac{\omega}{\mu}} \cos\left(\omega t + \frac{\pi}{4}\right). \quad (11)$$

The force on the whole plane surface is  $E = fS$ , where  $S$  is the area of the electrode surface. The corresponding amplitudes are

$$f_0 = \varepsilon \zeta E_0 \sqrt{\frac{\omega}{\mu}}, \quad F_0 = S \varepsilon \zeta E_0 \sqrt{\frac{\omega}{\mu}}. \quad (12)$$

Let, for example,  $E_0 = 1$  V/cm;  $\zeta = 0.1$  V;  $\omega/2\pi = 10^{-3}$  sec $^{-1}$ ;  $S = 0.5$  cm $^2$ ; for a diluted aqueous solution at 20°C  $\varepsilon = 80.3 \cdot 8.85 \cdot 10^{-14}$  F/cm;  $\mu = 0.01$  dyne · sec · cm/g. From (12)  $f_0 = 0.56 \cdot 10^{-2}$  dyne/cm $^2$  and  $F_0 = 0.28 \cdot 10^{-2}$  dyne.

In the case of  $|az| \gg 1$  we find from (10)

$$f = -\varepsilon E_0 d\psi/dz(0) \cos \omega t = q_s E_0 \cos \omega t, \quad (13)$$

where  $q_s$  is the charge of the unmoving lining of the double layer, i.e.,  $f = \bar{f}_k$ .

The correlations given above are obtained for an electrode with an even surface. Now let the surface be rough and the field inside the electrode and electrolyte far from the surface be oriented along the plane neutralizing the surface. Near the unevennesses the direction of the field varies and an alternating current is possible through the interface. The degree of influence of the current leakage on the electrophoresis is assessed by the ratio  $\kappa = j_{s0}/j_{b0}$ , where  $j_{s0}$  and  $j_{b0}$  are the amplitudes of the currents through a small section of the uneven surface of the electrode ( $j_{s0}$ ) and in the body of the electrolyte ( $j_{b0}$ ).

The  $j_{s0}$  current passes in the electrolyte between two points on the electrode surface with a distance between them smaller than the dimension of the unevenness along the surface  $d$  (for example, for a cylindrical surface with a periodic relief  $d$  is equal to the period). The amplitude of the potential  $\varphi_{s0}$  between these points satisfies the inequality  $\varphi_{s0} < E_0 d$ . The  $j_{s0}$  current overcomes successfully the resistance of the surface  $1/\omega C$  (twice) and of the electrolyte. Consequently  $j_{s0} < \varphi_{s0} \omega C/2$ . Here  $C$  is the specific capacity of the double layer. In the electrolyte  $j_{b0} = E_0/r$ , where  $r$  is its resistivity. By combining the inequalities we find

$$\kappa < \omega C r d/2. \quad (14)$$

Let, for example,  $r = 10^3 \Omega \cdot \text{cm}$ ;  $C = 100 \mu\text{F}/\text{cm}^2$ ;  $d = 10^{-5}$  cm;  $\omega/2\pi = 10^3$  sec $^{-1}$ . Then  $\kappa < 0.003$ . This result is true for the random factor of roughness  $\alpha$  since  $\alpha$  is related to the relative proportions of the relief and is independent of  $d$ . Thus, in practice the rough surface of the electrode is impermeable to current in a variable longitudinal field and the electrode behaves like a dielectric.

A certain parallel between the metal and a dielectric can also be drawn in the case of a transverse variable field. We shall examine three parallel metallic plates – a basic electrode placed in the gap between two auxiliary electrodes to which a sinusoidal voltage is applied. The space between the electrodes is filled with fluid (for example an electrolyte) or a gas. Changes in the charge density of opposing signs,  $\Delta q$  and  $-\Delta q$ , are induced at the opposing faces of the basic electrode. The surface tensions  $\gamma$  of these faces acquire increments of  $\Delta\gamma$  and  $-\Delta\gamma$ , corresponding to the magnitude of  $\partial\gamma/\partial q$  which is identical for both surfaces. The electrode reaches a state of flexural vibration enabling us to measure  $\partial\gamma/\partial q$ .

Moreover, the same increments in the charge  $\Delta q$  and  $-\Delta q$  are induced at the inner faces of the auxiliary electrodes. Let us now replace the basic electrode with a dielectric plate. The predetermined magnitude of  $\partial\gamma/\partial q$  with  $\Delta\gamma$  corresponding in a given case to the flexural vibration of the central plate and  $\Delta q$  referring to the auxiliary electrodes, can also be brought into conformity with it.

The simplest type of roughness is a wavy surface with unevennesses in the form of parallel ribs of isosceles triangular cross section. The roughness factor is  $\alpha = 1/\cos\varphi$ , where  $\varphi$  is the angle at the base of the triangle. Let the ribs be oriented across the field and let there be a fixed  $v_\tau = v_q \cos\varphi$  – the projection of the velocity  $v_q$  of the osmotic movement of the electrolyte near the true surface onto the plane neutralizing the

roughness. An approximate calculation of the viscous friction shows that as  $\vartheta$  rises from  $20^\circ$  to  $45^\circ$  ( $1.06 \leq \alpha \leq 1.41$ ) the velocity  $v_e$  in the body of the electrolyte falls from  $0.7v_T$  to  $0.4v_T$ . This makes it possible to find the attenuation coefficient of the electrophoretic force  $\beta = f_e/f$ , where  $f_e$  is the resultant along the plane neutralizing the roughness. For example, for a surface made up of sections of the type indicated with a random orientation relative to the field in the body

$$\beta \approx \frac{1}{2} \left( 1 + \frac{1}{\alpha} \right) \quad 1 \leq \alpha \leq 1.4 \quad (15)$$

#### LITERATURE CITED

1. N. A. Balashova and A. N. Frumkin, Dokl. Akad. Nauk SSSR, 20, 449 (1938).
2. S. S. Dukhin and B. V. Deryagin, Electrophoresis [in Russian], Nauka, Moscow (1976).
3. A. Ya. Gokhshtein, USSR Inventor's Certificate No. 206140, Byull. Izobr. No. 24 (1967).
4. A. Ya. Gokhshtein, Surface Tension of Solids and Adsorption [in Russian], Nauka, Moscow (1976).

### TWO-DIMENSIONAL CONDENSATION OF AN ORGANIC SUBSTANCE WITH REORIENTATION OF ADSORBED MOLECULES

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Based on the model of three capacitors in parallel, the shapes of adsorption isotherms and differential capacity curves were examined under conditions where the change in the orientation of adsorbed molecules leads to their two-dimensional condensation.

From the model of three capacitors in parallel [1], it follows that under certain conditions, which were formulated in general terms in [2], differentiation of the adsorption layer takes place. Under these conditions, the system of adsorption isotherms†

$$\left. \begin{aligned} B_1 c &= \frac{\theta_1}{n_1 (1 - \theta_1 - \theta_2)^{n_1}} \cdot \exp(-2n_1 a_1 \theta_1 - 2n_1 a_2 \theta_2) \\ B_2 c &= \frac{\theta_2}{n_2 (1 - \theta_1 - \theta_2)^{n_2}} \cdot \exp(-2n_2 a_2 \theta_2 - 2n_2 a_3 \theta_1) \end{aligned} \right\} \quad (1)$$

turns out to be multivalued, and a given concentration of organic substance  $c$  corresponds to three values of fractional surface coverage  $\theta_1$  and  $\theta_2$ . A more detailed analysis of the system of equations (1) was presented in [3, 4] for the special case  $n_1 = n_2 = 1$ . This case may be of interest for simultaneous adsorption of two organic substances. However, as a rule, under conditions of reorientation of adsorbed molecules from flat to vertical the surface area per adsorbed molecule decreases [1, 5, 6]. Under these conditions, from the physical point of view, the case where  $n_1 = 1$  and  $n_2 = 2$  (see Table II in [5]) is of great interest. Assuming, furthermore, that  $a_2 = a_3 = 0$  and introducing the notation  $a_1 = a$ ,  $B_1 c = c^*$ , and  $B_2/B_1 = k$ , from the system of isotherms (1), we obtain

$$c^* = \frac{\theta_1}{1 - \theta_1 - \theta_2} e^{-2a\theta_1} \quad (2a)$$

$$kc^* = \theta_2 / 2(1 - \theta_1 - \theta_2)^2 \quad (2b)$$

Solving Eq. (2b) for  $\theta_2$ , one obtains

$$\theta_2 = [4kc^*(1 - \theta_1) + 1 - \sqrt{8kc^*(1 - \theta_1) + 1}] / 4kc^* \quad (3)$$

†Notation is the same as in [1].

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