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The Motion of Solid and Liquid Metallic Bodies in Solutions of Electrolytes. I

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1. Electro-capillary motions of mercury

Christiansen[1] was the first to give a detailed description of the motions of drops of mercury under the influence of an electric current. After a number of older qualitative observations he showed that when an electric current passes through a drop of mercury in an electrolyte solution the potential difference across the mercury-solution interface changes, inducing changes in the boundary layer. If the mercury in the solution initially carried a positive charge, the interfacial tension increases at the point where the current enters the drop (negative pole of the drop) and decreases at its point of egress (positive pole). These changes in the interfacial tension cause the mercury to move from the positive to the negative pole along the surface and in the opposite direction within the drop itself. The moving mercury surface drags along the adjacent layers of the solution, as a result of which the drop as a whole effects a reaction movement along the lines of current. This motion, named electrocapillary motion by Christiansen, can be observed, for example, in the deviation from the vertical of mercury drops falling in an electric field. The velocity of the motion is very great, considerably exceeding that of the ordinary electrokinetic motions. As the solution is diluted, the velocity of the drop in the field, calculated for the same potential gradient, decreases. Besides the motion of the drop as a whole, Christiansen described the changes in form which it undergoes.

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[1] Christiansen, Ann. Phys. (4), **12**, 1072 (1903).

The curvature decreases at the positive pole and increases at the negative pole, so that the drop advances with its obtuse end.

It follows from the theory of electrocapillarity that the motion of the drop in the field should cease if its initial potential corresponds to the maximum of the electrocapillary curve, *i. e.* to the point of zero charge. This conclusion was confirmed by Frumkin[2] for falling drops, and by Bodforss[3] and Craxford[4] for drops at rest on a glass surface.

The motions of mercury drops in an electric field were first investigated theoretically by Craxford, Gatty and Mackay[4]. These authors came to the conclusion that the electrophoretic force acting on a drop is equal to the product of the electric field intensity by the charge of the inner sheet of the double layer, the latter quantity being measured by the usual electrocapillary methods. It is obvious, however, that the sum of the electric forces, acting on a system of total charge equal to zero, cannot itself be different from zero, so that the conclusion in this form is incorrect. These authors consider the motions of mercury drops at small potential gradients as a particular case, and the simplest one, of ordinary electrophoresis. Besides observations on the motions of comparatively large drops, the literature also contains data on the electrokinetic behaviour of mercury droplets of colloidal dimensions (10^{-4}cm) in mercury sols in the presence of small concentrations of electrolyte[5]. The observed velocities do not differ in order of magnitude from those common in electrokinetic motions.

N. Bach[6] investigated in the laboratory of A. Frumkin the potential differences which arise when a shower of mercury droplets falls in a column of electrolyte, *i. e.* an effect similar to the currents caused by the fall of solid particles in liquids (Dorn effect), the theory of which has been given by Smoluchowski[7]. However, the potential differences induced by mercury droplets falling in a normal KNO_3

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[2] Frumkin, J. Russ. Chem. Soc., **49**, 207 (1917).

[3] Bodforss, Z. Elektrochem., **29**, 127 (1923).

[4] Craxford, Phil. Mag., **16**, 268 (1933); Craxford, Gatty and Mackay, Phil. Mag., **23**, 1079 (1937).

[5] Nordlund, Koll. Z., **26**, 121 (1920); Bull u. Söllner, ibid., **60**, 263 (1932).

[6] N. Bach, Acta Phys. Chim., **1**, 27 (1934).

[7] Smoluchowski in Graetz, Handb. der Elektrizität und des Magnetismus, **2**, 385 (1914).

solution are about 10^5 times greater than the possible values for solid particles; in a 10^{-5} normal KNO_3 solution the ratio is approximately 10 : 1. Thus, the observed potential differences, especially in well conducting solutions, cannot be interpreted as ordinary electrokinetic effects. This phenomenon can be explained as a reversal of the Christiansen effect. As the drop falls through the solution the surface of the mercury carrying the charges of the double layer is pushed back, thus diminishing the charge density of the double layer on the front part of the drop and increasing it at its rear. This leads to potential differences in the electrolyte between the ends of the drop and, hence, induces currents.

Interest in electrocapillary movements increased in connection with the problem of the so-called polarographic maxima on the current—voltage curves for a mercury electrode, discovered and described by Heyrovsky and co-workers.

It has been shown by Frumkin and Bruns[8] that the high values of the current observed at these maxima are due to the solution being stirred by the electrocapillary motions of the mercury surface. We shall not dwell on the theory of polarographic maxima at any length in the present paper, inasmuch as we hope shortly to discuss the problem in a separate publication. The electrocapillary motions giving rise to these maxima were subsequently extensively investigated for both the case of a mercury electrode with constant surface area[9], and for a dropping electrode, the latter, in particular, by Antweiler and Stackelberg[10]. Antweiler considers that the motions of the mercury surface are electrokinetic, and that they attain considerable velocities due to the absence of such large frictional drags, as at solid surfaces, and to the mobility of the charges in the inner sheet of the double layer

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[8] Frumkin and Bruns, Acta Phys. Chim., **1,** 232 (1934); see also Kolthoff and Lingane, Polarography, New York, 1943, p. 113 and foll.

[9] Bruns, Frumkin, Jofa, Vanjukova and Zolotarevskaja, Acta Phys. Chim., **9,** 359 (1938); Jofa and Frumkin, C. R. Acad. Sci. URSS, **20,** 213 (1938); Jofa, Losev and Tretjakov, J. Phys. Chem. (russ.), **19**, 358 (1945).

[10] Seidell, Z. angew. Chem., **48,** 463 (1935); Stackelberg, Antweiler u. Kieselbach, Z. Elektrochem., **44,** 663 (1938); Antweiler, Z. Elektrochem., **44,** 719, 831, 888 (1938); Stackelberg, ibid., **45,** 490 (1939).

caused by the high electrical conductivity of mercury. In contrast to electrokinetic motions at a solid surface, the double layer at the mercury surface moves as a whole. Antweiler regards it as essential for the phenomenon that the current pass through the solution—metal interface. This latter circumstance is especially emphasized in Stackelberg's review. According to Stackelberg the motions described by Christiansen are connected with the presence of dissolved oxygen in the solution. If the oxygen is completely removed, *i. e.* in the case of an ideally polarizable droplet, the motions should cease.

Krjukova and Kabanov[11] called attention to the motions which arise in a solution near the surface of dropping mercury caused by the process of dropping itself. They found that these motions are observed particularly well at comparatively high concentrations of the electrolyte (above 0.1 N).

The papers cited do not throw sufficient light on the questions concerning the influence of the electrolyte on the motion of the mercury surface, the hydrodynamical properties of this surface in conducting solutions and the relations between electrocapillary and electrokinetic motions. Whereas the majority of authors dealt with these two groups of phenomena as having no bearing on one another and this viewpoint is followed out in the principal monographs on the subject, Craxford, Gatty and Mackay[4], as has already been observed, do not distinguish between the electrocapillary motions and the ordinary electrokinetic motions of solid particles. The difficulties here involved become even more evident in the theory of polarographic maxima. The aim of the present paper is to establish the principal relationships governing these phenomena.

We shall limit ourselves at first to a consideration of the motions of a mercury surface in the case when the latter is not an electrode, *i. e.* when the algebraic sum of all the charges appearing and disappearing on the entire surface is zero. The motions on a mercury electrode will be considered subsequently. In order to make the problem clearer, we shall briefly review the physical fundamentals of the theory of electrokinetic phenomena, limiting ourselves, however, to its elementary part which we shall need for comparison with the theory of electrocapillary phenomena.

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[11] Krjukova and Kabanov, J. Phys. Chem. (Russ.) **13**, 1454 (1939); **15**, 475 (1941).

2. Electrokinetic motions of non-conducting particles

If a solid spherical particle of radius a and surface charge e in a non-conducting liquid of viscosity μ is subjected to the action of an electric field of intensity E, its velocity U, in the case of «slow» (Stokes) motion, is equal to

$$U = \frac{eE}{6\pi\mu a} = \frac{2\varepsilon E a}{3\mu}, \tag{1}$$

where ε is the surface density of charge. In the case of a liquid particle the expression for U will have a slightly different numerical coefficient. Expression (1), however, is not valid for a particle in an electrolyte solution. In this case, as is well known, the velocity of the particle is

$$U = \frac{D\zeta E}{4\pi\mu}, \tag{2}$$

where E is the electric field intensity at a great distance from the particle, D—the dielectric constant of the medium and ζ—a certain effective potential difference between the particle and the solution, which is usually called the electrokinetic (zeta) potential. If instead of ζ we introduce the average thickness d of the double layer, determined by the relation:

$$4\pi\varepsilon d = D\zeta, \tag{3}$$

then equation (2) takes the form:

$$U = \frac{\varepsilon E d}{\mu}, \tag{2'}$$

where ε, as formerly, is the surface density of charge.

The theory of electrokinetic motions was developed by Helmholtz and Smoluchowski[12]. In the derivation of equation (12) it is assumed that the external field is additively superimposed on the field of the double layer, and that the thickness of the double layer is small as compared with the dimensions of the particle. We shall limit ourselves in what follows to the case when the latter condition obtains.

The velocity calculated by equation (3) is less in order of magnitude than that according to equation (1) by a factor of the order of d/a. This is due to the circumstance that in electrolytic solutions the surface of the particle no longer carries a free charge, but is surround-

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[12] Smoluchowski, loc. cit., pp. 366—428.

ed by an electric double layer of positive and negative charges in equal amounts. The force acting per unit area of each sheet is equal in magnitude to εE_y, where E_y is the component of the field intensity tangential to the particle surface. But the forces acting on the two sheets are opposite in sign and since their points of application are a very small distance d apart, the viscous drag acquires a large value, and the velocity of motion is small. Whereas for a particle carrying free charges the frictional drag (per unit surface) is of the order of $\mu U/a$, in electrokinetic motion its magnitude is of the order of $\mu U/d$.

Smoluchowski drew attention to the essential correction which must be introduced into the electrokinetic equations when the body is in a poorly conducting medium. In this case, the convection current due to the relative motion of the outer sheet of the double layer is superimposed on the ordinary current of bulk conductivity and distorts the field. In the limiting case when the current of bulk conductivity near the particle can be disregarded in comparison with the surface convection current, the velocity of the particle is determined from the condition that the current of bulk conductivity at a great distance from the particle goes over into the surface current at its boundary.

Under these conditions we have for a spherical particle (see below):

$$U = \frac{a\varkappa E}{\varepsilon}\,. \tag{4}$$

Usually the surface conductivity was taken into account simply as a correction to equation (2) or (3)[12]. A consideration of surface convection conductivity in the case of a spherical particle brings to the following expression, derived by B. Levich (Part III to appear shortly):

$$U = \frac{\varepsilon E d}{\mu + \frac{d\varepsilon^2}{a\varkappa}}\,. \tag{5}$$

If $d\varepsilon^2/a\varkappa\mu \ll 1$ (usual case), equation (5) goes over into (3); if $d\varepsilon^2/a\varkappa\mu \gg 1$, equation (5) goes over into (4). Since the velocity of the outer sheet of the double layer at a potential gradient equal to unity is $\varepsilon : \frac{\mu}{d}$, the quantity $d\varepsilon^2/\mu$ expresses the specific surface conductivity, while $d\varepsilon^2/a\varkappa\mu$ in order of magnitude represents the ratio of the convection current on the surface of the particle to the bulk conductivity current in a conductor of cross section determined by the linear dimensions of the particle.

The theory of surface conductivity was developed by a number of authors, in particular, by Bikerman[13] and Hermans[14]. Bikerman pointed out that, in addition to convective surface conductivity, it is necessary to take into account the surface electrical conductivity connected with the presence of an excess of ions adsorbed on the particle surface. Thus, if $\varepsilon = 0$ but the surface carries equal amounts of adsorbed cations and anions, the surface electrical conductivity will evidently be equal to

$$\Gamma F\,(U_c + U_a),$$

where Γ is the quantity adsorbed in equivalents per unit area, U and U_a—the mobilities of the cation and anion, respectively, in the surface layer. In the case of motion near a solid wall this effect should be of the same order of magnitude as the convection effect. Indeed, the ratio $\frac{\varepsilon^2 d}{\mu} : \Gamma F\,(U_c - U_a)$ is of the order of $\zeta : \frac{e_0}{r_0 D}$, where e_0 and r_0 are the charge and radius of the ion respectively, D—the dielectric constant of the medium, and $\zeta : \frac{e_0}{r_0 D} \sim 1$. One cannot, however, agree to the validity of Bikerman's method of computation, in which the total surface electrical conductivity is taken simply as equal to the sum of the convection and conduction terms. That such an assumption is not permissible becomes clear as soon as one considers the case of a surface layer containing practically ions of only one sign, for example, cations. In this case, according to Bikerman, the quantity of electricity transported by the charges in the surface layer in a field of unit intensity should be equal (in our notation) to $\int\limits_0^\infty \varepsilon_x (U_c + V_x)$, where ε_x and V_x are, respectively, the charge density and the velocity of the liquid at a distance x from the wall. It is evident, however, that in reality, when the distances between ions of like sign are on the average small compared with the distances of the ions from the wall, the liquid medium should move together with the ions as a whole and the quantity of electricity

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[13] Bikerman, Z. physik. Chem., (A), **163,** 378 (1933); **171,** 209 (1934); Trans. Farad. Soc., **36,** 154 (1940).

[14] Hermans, Phil. Mag., **26,** 650 (1936).

transported should equal $\int\limits_0^\infty \varepsilon_x V_x dx$, or, for a linear distribution of potential $\varepsilon^2 d/\mu$. In the opposite case, when the distances between the ions are large compared with the distances of the ions from the wall, the quantity of electricity transported sould be equal to $\int\limits_0^\infty \varepsilon_x U_x dx$ where U_x, the mobility of the cation, is slightly changed by the neighbourhood of the wall. In the general case, the surface conductivity should lie between these two values, rather than be equal to their sum, as Bikerman assumes. In the equations that figure in the present paper only the convection term is taken into account, inasmuch as our purpose is to draw a comparison with the equations of electrocapillary motions. In the latter case, as will be shown later, the convective conductivity is larger than the conduction term by several orders of magnitude.

Hermans considers in his investigation the polarization of a double layer by an applied electric field. His boundary condition for the charge density is, however, incorrect. He puts the change in the density of the particle surface charge equal to zero, whereas in reality, the boundary condition is that the normal component of the current be zero. As regards the charge density, computation shows that its variation by no means vanishes on the surface. The conclusions of the paper discussed cannot, therefore, be accepted.

Among the other electrokinetic phenomena which we shall consider in the present paper, besides the motion of a particle in an electric field, special interest is presented for us by the currents caused by the motions of particles in a liquid, in particular, by the fall of particles under the influence of gravity. In this case the motion of the particle displaces one sheet of the double layer with respect to the other, and the free charges of opposite sign which appear at the ends of the particle are neutralized by a conduction current in the bulk of the liquid. According to Smoluchowski, the potential difference E per unit length of tube appearing on sedimentation of suspended spherical particles, equals

$$E = \frac{d\varepsilon P n}{\mu \varkappa} \tag{6}$$

(E being expressed in terms of ε, and not of ζ, as done by Smoluchowski), where P is the weight of a particle in the liquid and n—the number of particles per unit volume. In the case of low bulk conductivity, equation (6) stands in need of a correction, analogous to Smoluchowski's correction for surface conductivity in the expression for the currents which arise when a liquid flows through a capillary. Physically this means that the potential difference resulting from the motion of the particles tends to make the outer sheet of the double layer move in a direction opposite to that of the imposed motion; in other words, the potential difference is counteracted by both bulk and surface conductivity. In the limiting case the potential differences can be determined from the condition that the electric field induced by the fall of the particle completely hinders the relative displacement of the outer sheet caused by the viscosity drag. In this case, instead of (6) (see below) we have

$$E = \frac{aPn}{\varepsilon} \tag{7}$$

The general expression for E has the form:

$$E = \frac{d\varepsilon Pn}{\mu\varkappa + \frac{d}{a}\varepsilon^2}. \tag{8}$$

The transition to both limiting cases (6) and (7) is determined, as in cataphoresis, by the value of the dimensionless quantity $\frac{d}{a} \cdot \frac{\varepsilon^2}{\mu\varkappa}$. The difference between the expressions (2′) and (6), on the one hand, and (4) and (7), on the other, consists in that the former imply that the potential difference is neutralized by bulk conductivity, whereas in the derivation of the latter it is assumed that near the particle surface this effect is entirely due to the migration of the outer sheet of the double layer. If we consider the effects described by the general equations (5) and (8) in their dependence on ε we come to the unexpected conclusion that with an increase in ε, the quantities U in (5) and E in (8) pass through a maximum at $\varepsilon = \left(\frac{a\mu\varkappa}{d}\right)^{\frac{1}{2}}$ and thereafter decrease. Unfortunately, this conclusion cannot be verified on the experimental material available.

3. The system of forces acting on the surface of a conducting particle

The influence of conductivity on electrokinetic phenomena was investigated by Henry[15]. However, for a metallic particle, *i. e.* for a particle whose electrical conductivity considerably exceeds the conductivity of the solution, the cataphoretic velocity calculated from his formulae becomes zero. As shown by both Henry and other authors[16] this is due to neglect of polarization phenomena in the deduction. If the particle is sufficiently polarizable, so that the lines of current cannot pass through it, its behaviour should evidently approach that of a non-conducting body. In the available literature, however, we can find no quantitative discussion[17] of the rôle of polarization phenomena in the cataphoresis of metallic particles. In this paragraph we shall consider the forces acting on a spherical metallic particle in a solution of electrolytes under action of an electric field. We shall assume at first that the particle is ideally polarizable, *i. e.*, that the potential differences at the solution — metal interface prevent both the discharge of ions of the solution and the formation of new ions. Under these conditions the normal component of the current at the surface of the particle, and, therefore, the normal component of the field in the solution outside the double layer is zero, in other words, the distribution of the lines of force outside the double layer is the same as in the case of a non-conducting body. We also assume, for the time being, that the double layer has a Helmholtz structure, *i. e.*, that the centres of gravity of the ions forming the outer sheet of the double layer lie on the surface of a sphere of radius $a+d$, concentric with the surface of the particle. It is usually assumed that the outer sheet of the Helmholtz double layer is rigidly bound with the surface of the metal. One might consider, however, that the surface of the metal is covered with a layer of adsorbed molecules, which plays the part of the dielectric in the double layer, keeping the contra-ions at a constant distance from the surface of the metal in such a way that they retain their mobility. Regardless of the soundness of such

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[15] Henry, Proc. Roy Soc., (A), **133**, 106 (1933).

[16] Verwey u. Kruyt, Z. physik. Chem., **167**, 137 (1933); Kruyt u. Oosterman, Kolloidchem. Beih., **48**, 377 (1938).

[17] The paper of Overbeck, C. B. I, 2673 (1943), was unfortunately not available.

an assumption, we shall here utilize the simple Helmholtz model of the double layer to investigate the electrokinetic behaviour of metallic particles, as providing the best illustration of the relations under discussion. The distribution of the lines of force in the case of a positively charged particle conforming to our assumptions is shown in Fig. 1. The Y axis has been taken parallel to the lines of force at a great distance from the particle. Denote by E the field intensity far from the particle, by r—the distance to the centre of the sphere, by θ—the angle between the radius vector and the y axis $(0 \leqslant \theta \leqslant \pi)$. The zero value of the potential in the solution is chosen at $r=a+d$ and $\theta=\pi/2$. Then at $r \geqslant a+d$

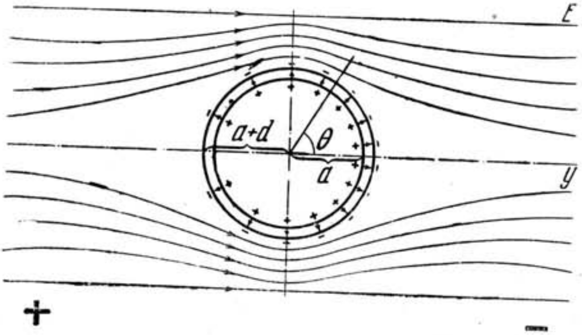

Fig. 1. An «ideally polarizable» positively charged particle in an electric field. The arrows show the direction of the applied field and of the field of the double layer.

$$\varphi = -E\left\{r + \frac{1}{2}\frac{(a+d)^3}{r^2}\right\}\cos\theta \tag{9}$$

and at $r=a+d$

$$\varphi = -\frac{3}{2}E(a+d)\cos\theta. \tag{9a}$$

Inside the metal and on its surface, *i. e.* at $r \leqslant a$

$$\varphi = \varphi_0, \tag{9b}$$

where φ_0 is a constant. The solution of the Laplace equation satisfying the boundary conditions (9a) and (9b) has the form

$$\varphi=\varphi_0\left(\frac{a+d}{r}-1\right)\frac{a}{d}-\frac{3}{2}\,\frac{E\cos\theta}{1-\left(\frac{a}{a+d}\right)^3}\left(r-\frac{a^3}{r^2}\right). \qquad (9c)$$

Equations (9), (9a), (9b) and (9c) can serve to determine the quantities characterizing the double layer, in particular, the forces acting on it.

We introduce the following notations: $\Delta\varphi$ — potential jump between the metal and the solution in the double layer; ε — charge per unit area of the inner sheet of the double layer, ε' — charge per unit area of the outer sheet, E_t — field intensity component tangential to the surface of the double layer (E_t is considered positive when it forms an acute angle with the y axis); E_{n_1} — field component normal to the surface at the boundaries of the double layer, and E_{n_2} — the same when the normal is directed out of the double layer. To compute the forces we choose a part of the double layer consisting of a surface element of the inner sheet, dS, and a surface element of the outer sheet $\frac{(a+d)^2}{a}\,dS$ included in the same solid angle. We denote by $F_t\,dS$ the tangential force on this element, and by $F_n\,dS$ — the normal force, the positive direction of F_t being taken the same as the positive direction of E_t and the positive direction of F_n being towards the centre of the sphere (Fig. 2).

In determining the values of the above quantities we shall assume that $d \ll a$, and shall limit ourselves in all the final expressions to the first term of the development of the power series in d/a. In order to obtain these results, however, it is necessary to determine the intermediate values of E_n and ε with an accuracy up to terms of the next order.

From equations (9) — (9c) it follows that

$$\Delta\varphi=\varphi_0+\frac{3}{2}Ea\cos\theta. \qquad (10)$$

The density distribution of the lines of force in the double layer, schematically depicted in Fig. 1, corresponding to the dependence of $\Delta\varphi$ on θ, (for $\Delta\varphi>0$), visualizes the polarization of the double layer under the influence of an external field.

Further,

$$(E_{n_1})_{r=a} = -\left(\frac{\partial\varphi}{\partial r}\right)_{r=a} = \varphi_0\left(\frac{1}{d}+\frac{1}{a}\right)+\frac{3}{2}\,Ea\cos\theta\,\left(\frac{1}{d}+\frac{2}{a}\right), \tag{11}$$

$$\begin{aligned}(E_{n_1})_{r=a+d} &= \left(\frac{\partial\varphi}{\partial r}\right)_{r=a+d} = \\ &= -\varphi_0\left(\frac{1}{d}-\frac{1}{a}\right)-\frac{3}{2}\,Ea\cos\theta\,\frac{1}{d},\end{aligned} \tag{11a}$$

where the values of $\partial\varphi/\partial r$ are determined from equation (9c).

$$(E_{n_2})_{r=a} = (E_{n_2})_{r=a+d} = 0, \tag{11b}$$

$$(E_t)_{r=a} = 0, \tag{12}$$

and

$$(E_t)_{r=a+d} = \frac{1}{a+d}\left(\frac{\partial\varphi}{\partial\theta}\right)_{r=a+d} = \frac{3}{2}\,E\sin\theta, \tag{12a}$$

$$\begin{aligned}\varepsilon &= \frac{k}{4\pi}\{(E_{n_1})_{r=a}+(E_{n_2})_{r=a}\} = \\ &= \frac{k}{4\pi}\left\{\varphi_0\left(\frac{1}{d}+\frac{1}{a}\right)+\frac{3}{2}\,Ea\cos\theta\,\left(\frac{1}{d}+\frac{2}{a}\right)\right\},\end{aligned} \tag{13}$$

$$\begin{aligned}\left(\frac{a+d}{a}\right)^2\varepsilon' &= \frac{k}{4\pi}\{(E_{n_1})_{r=a+d}+(E_{n_2})_{r=a+d}\}\left(\frac{a+d}{a}\right)^2 = \\ &= -\frac{k}{4\pi}\left\{\varphi_0\left(\frac{1}{d}+\frac{1}{a}\right)+\frac{3}{2}\,Ea\cos\theta\,\left(\frac{1}{d}+\frac{2}{a}\right)\right\} = -\varepsilon,\end{aligned} \tag{13a}$$

where k is the dielectric constant of the medium in the double layer.

From equations (11), (12) and (13) it is easy to determine the quantities F_t and F_n. Retaining in the final expression only the first of the development in power series, we obtain:

$$F_t = (E_t)_{r=a}\,\varepsilon + (E_t)_{r=a+d}\,\varepsilon'\left(\frac{a+d}{a}\right)^2 = -(E_t)_{r=a+d}\,\varepsilon, \tag{14}$$

and hence

$$\begin{aligned}F_t &= -\frac{k}{4\pi d}\left\{\varphi_0+\frac{3}{2}\,Ea\cos\theta\right\}\frac{3}{2}\,E\sin\theta = \\ &= \frac{1}{a}\,C\Delta\varphi\,\frac{\partial\varphi}{\partial\theta} = \frac{1}{a}\,\frac{\partial\Delta\sigma}{\partial\theta},\end{aligned} \tag{14a}$$

where $C=\frac{k}{4\pi d}$ is the capacity of the double layer per unit area under the condition $d \ll a$, and $\Delta\sigma=\frac{C}{2}(\Delta\varphi)^2$. It is well known that in the case of a Helmholtz double layer the quantity $\Delta\sigma$ expresses the lowering of the interfacial tension due to the surface charges. The direction of the force F_t is shown in Fig. 2.

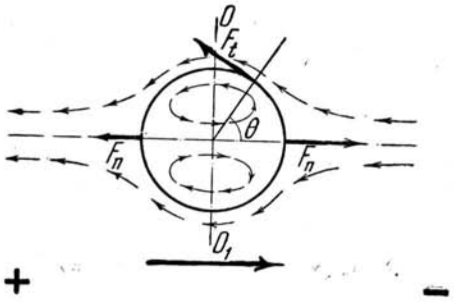

Fig. 2. The motion of a positively charged particle in an electric field. The small arrows denote the direction of motion of the liquid, the thick arrows—the direction of the forces, the large arrow in the lower part of the figure—the direction of motion of the particle as a whole, F_n is the electrical component of the normal force.

For the normal component

$$F_n = -\frac{1}{2}\left\{ (E_{n_1})_{r=a} - (E_{n_2})_{r=a} \right\} \varepsilon + \\ + \frac{1}{2}\left\{ (E_{n_1})_{r=a+d} - (E_{n_2})_{r=a+d} \right\} \left(\frac{a+d}{a}\right)^2 \varepsilon' = \\ = -\frac{C(\Delta\varphi)^2}{a} = -\frac{2\Delta\sigma}{a}. \qquad (15)$$

It is evident from (15) that the absolute value of F_n is larger on the right-hand side of the sphere than on the left-hand side. The direction and relative values of F_n for $\theta=0$ and $\theta=\pi$ are shown in Fig. 2.

From equations (14) and (15) we find the resulting forces which act on the particle as a whole. The force F_t has a component parallel to the y axis equal to $F_t \sin\theta$; the tangential component acting on the portion of the double layer between the angles θ and $\theta+d\theta$ is, therefore, equal to

$$2\pi a^2 \sin\theta\, d\theta\, F_t \sin\theta = 2\pi a \sin^2\theta \frac{\partial\Delta\sigma}{\partial\theta}\, d\theta =$$
$$= -3\pi a^2 EC \sin^3\theta \left(\varphi_0 + \frac{3}{2} Ea\cos\theta\right) d\theta.$$

For the force on the whole surface we obtain:

$$-\int_0^\pi 3\pi a^2 E \sin^3\theta C \left(\varphi_0 + \frac{3}{2} Ea\cos\theta\right) d\theta = -4\pi a^2 C\varphi_0 E =$$
$$= -4\pi a^2 \varepsilon_0 E = -e_0 E, \tag{16}$$

where $\varepsilon_0 = C\varphi_0$ is the charge density on the surface of the metal in the absence of an external field, and $e_0 = 4\pi a^2 \varepsilon_0$ is the total charge of the surface. Thus the forces operative on the double layer tangent to the surface of the metal have a component parallel to the field intensity, equal in magnitude to the force acting on a particle with a free charge e_0 but opposite in sign, inasmuch as they originate from the charges of the outer sheet of the double layer.

The component of the force F_n parallel to the y axis equals $F_n \cos\theta$. Integrating over the surface of the particle we obtain:

$$-\int_0^\pi 2\pi a^2 \sin\theta F_n \cos\theta d\theta = 4\pi a \int_0^\pi \Delta\sigma \sin\theta \cos\theta d\theta =$$
$$= 4\pi a^2 C\varphi_0 E = e_0 E. \tag{17}$$

Thus, the sum of the tangential and normal forces acting on the double layer is zero, as was to be expected. Another result obtains, however, if one does not consider the entire surface of the particle, but only a part of it, *e. g.* a spherical segment determined by the angles θ and $\pi - \theta$ (Fig. 1). The sum of the forces parallel to the y axis is evidently equal to:

$$2\pi a^2 \int_\theta^{\pi-\theta} (F_t \sin^2\theta - F_n \sin\theta\cos\theta)\, d\theta =$$
$$= 2\pi a \int_0^{\pi-\theta} \left(\sin^2\theta \frac{\partial\Delta\sigma}{\partial\theta} + 2\Delta\sigma \sin\theta\cos\theta\right) d\theta =$$
$$= 2\pi a \left| \Delta\sigma \sin^2\theta \right|_\theta^{\pi-\theta} = \frac{3}{2} e_0 E \cos\theta \sin^2\theta. \tag{18}$$

This expression vanishes at $\theta = 0$, as follows from the preceding; its magnitude passes through a maximum equal to $e_0 E/\sqrt{3}$

at $\cos^2\theta = {}^1/_3$. A part of the particle surface consisting of two spherical layers, one subtended by the angles 0 and θ, and the other by $\pi-\theta$ and π is acted upon by a force equal in magnitude and opposite in sign to the above value; under the influence of these forces stresses should arise in a solid metallic particle which are absent in the case of a non-conducting particle. In a liquid metallic particle these same forces, whose points of application are separated by distances of the order of the particle radius, must give rise to motions far more intense than the usual electrokinetic motions. The above derivation, which is based on a consideration of the electric forces operating on the charges in the simplest model of a double layer, is somewhat involved and not sufficiently general. The same results could be obtained in the general case much more rapidly by introducing the concept of interfacial tension from the very beginning. However, inasmuch as this concept does not figure in the usual theory of electrokinetic motions, we should thus be introducing a difference in the treatment of electrokinetic and electrocapillary motions.

The preceding derivation shows that this difference is of no fundamental importance and that the results here obtained also follow necessarily from the application of the method which in the case of a non-conducting particle brings to the usual theory of electrokinetic motions. We shall now show how the equations deduced follow from the concept of an interfacial tension between the metal and the solution.

Let us assume that the gradient of the electric field at the metal surface outside the double layer is small compared with its value in the layer normal to the surface, so that the concepts of potential and field intensity near the particle surface but outside the double layer have a definite meaning. Assume also that the radius of the particle is sufficiently large, so that the interfacial tension is independent of it. Under these conditions the state of the surface layer and, hence the metal—solution interfacial tension σ at each point of the metal surface is uniquely determined by the potential difference between the metal and the solution $\Delta\varphi = \varphi_0 - \varphi_e$, where φ_e is the value of the potential in the solution at the metal surface but outside the double layer. Or, inasmuch as $\varphi_0 = \text{const}$, σ is determined by the quantity φ_e and is independent of the potential difference at the neighbouring points. If $\Delta\varphi$ were constant, σ would also be constant, and no tangential forces would arise on the surface of the metal. In the case of a polarized particle $\Delta\varphi$, and, hence, σ vary from point to point. The tangential force acting on the surface is given in magnitude and direction by grad $\sigma \cdot dS$; and, since σ depends only on θ and F_t is considered positive if the tangential force is directed towards the decreasing values of θ, we have

$$F_t \, dS = -\frac{1}{a}\frac{\partial\sigma}{\partial\theta}\, dS. \tag{19}$$

From equation (19) and the Lippman—Helmholtz equation

$$\frac{\partial\sigma}{\partial\Delta\varphi} = -\varepsilon$$

it follows that

$$F_t = -\frac{1}{a}\frac{\partial\sigma}{\partial\theta} = -\frac{1}{a}\frac{\partial\sigma}{\partial\varphi_e}\cdot\frac{\partial\varphi_e}{\partial\theta} = -\frac{\partial\sigma}{\partial\Delta\varphi}E_t = -\varepsilon E_t. \tag{20}$$

Equation (20) is a generalization of (14) and since $\sigma = \sigma_0 - \Delta\sigma$, where σ_0 is the value of the interfacial tension at the maximum of the electrocapillary curve and $d\sigma = -d\Delta\sigma$, equation (19) is a generalization of (14a).

The force F_n normal to the surface, according to the Laplace formula of capillary pressure, is equal to

$$F_n = \frac{2\sigma}{a} = \frac{2\sigma_0}{a} - \frac{2\Delta\sigma}{a}. \tag{21}$$

Equation (21) differs from (15) by the constant term $2\sigma_0/a$ which could not appear in the latter, since only forces of electrical origin were considered in its derivation, their direction being given in Fig. 2. Return once more to a consideration of the forces acting on a part of the surface between the angles θ and $\theta + d\theta$. The resultant of all the surface tensions acting on this element is evidently directed along the y axis and equals

$$\begin{aligned} &-\frac{\partial}{\partial\theta}(2\pi a\sigma\sin^2\theta)\,d\theta = \\ &= -2\pi a\sin^2\theta\,\frac{\partial\sigma}{\partial\theta}\,d\theta - 2\pi a^2\sin\theta\times\cos\theta\times 2\,\frac{\sigma}{a}\,d\theta = \\ &= F_t\sin\theta dS - F_n\cos\theta dS. \end{aligned} \tag{22}$$

The first term in expression (22) gives the projection of the tangential forces, the second term — the projection of the normal forces on the y axis. In integrating over the entire surface of the sphere the quantity F_t, $\sin\theta$ does not change in sign; but the quantity $F_n \cos\theta$ has opposite signs in the two hemispheres separated by the plane OO' (Fig. 2). However, inasmuch as the value of the surface tension (at $\varepsilon > 0$) in the left hemisphere is greater than in the right one the resultant of all the normal forces is positive and exactly cancels out the resultant of all the tangential forces, for, according to equation (22),

$$\int_0^\pi F_n \cos\theta dS = \int_0^\pi F_t \sin\theta dS.$$

In the absence of a field, *i. e.* when $\sigma = \text{const}$, each of these integrals vanishes, and all the forces reduce to a uniform compression $2\sigma_0/a$.

The deduction based on the thermodynamic Lippman — Helmholtz equation has the advantage of generality. An essential shortcoming of the procedure, however, consists in that it yields only the resultant tangential force, which is insufficient, for example, when we wish to consider the electrokinetic motions of a solid particle.

Let us now find the force $(F_t)_x$ acting at a distance x from the metal — solution interface in the case of a Gouy diffuse double layer. We shall limit ourselves to the case of a plane interface $x = 0$ (*i. e.* a sufficiently large particle, whose curvature may be neglected), inasmuch as the transition from a plane to a spherical particle introduces nothing new with respect to the Helmholtz layer discussed above. In the case of a plane interface the field intensity in the electrolyte outside the double layer can be considered constant. Denote by E_t, as above, the field intensity parallel to the metal surface at a distance which is great compared to the thickness of the double layer. Let the positive direction of the x axis be directed into the solution perpendicular to the metal surface, and let $\varphi = 0$ at $y = 0$ and sufficiently large x. Then, outside the double layer $\varphi = -E_t y$. Upon application of an external electric field, equilibrium in the double layer is destroyed and a current flows through it. On the surface of an ideally polarizable particle, however, the normal component of the current is zero. The equation of continuity for the current is of the form:

$$\frac{\partial j_x}{\partial x} + \frac{\partial j_y}{\partial y} = 0. \tag{23}$$

and inasmuch as all the gradients parallel to the wall are small compared to the perpendicular ones,

$$\frac{\partial j_x}{\partial x} = 0 \quad \text{or} \quad j_x = \text{const} = 0.$$

Hence, for a sufficiently large particle whose curvature can be neglected, one may assume that the equilibrium is undisturbed and write the differential equation of the diffuse layer (for a uni-univalent electrolyte) in the form

$$\frac{k}{4\pi}\frac{\partial^2 \varphi}{\partial x^2} = -Fc\left\{ e^{-\frac{(\varphi + E_t y)F}{RT}} - e^{\frac{(\varphi + E_t y)F}{RT}} \right\}, \tag{24}$$

where c is the concentration of the solution.

As in equation (23), we have neglected the differential coefficients perpendicular to the wall. The component of the electric force parallel to the metal surface, acting on a volume element of the diffuse part of the double layer lying between y and $y + dy$ with the base 1 cm², is equal to $(E_t)_x \varepsilon_x \, dx$, where $(E_t)_x$ is the tangential component of the field and ε_x the charge density at a distance x from the interface:

$$(E_t)_x \varepsilon_x \, dx = \left(\frac{\partial \varphi}{\partial y}\right) \cdot \frac{k}{4\pi} \frac{\partial^2 \varphi}{\partial x^2} \, dx.$$

In addition, there is an osmotic pressure gradient in the polarized diffuse double layer, since the ion concentration varies from point to point; this gives a ponderomotive force equal to $-\frac{\partial p_x}{\partial y}\,dx$, where p_x is the osmotic pressure at a distance x from the interface. The resultant ponderomotive force $(F_t)_x \, dx$ is thus equal to

$$(F_t)_x \, dx = \frac{k}{4\pi}\frac{\partial \varphi}{\partial y} \cdot \frac{\partial^2 \varphi}{\partial x^2}\, dx - \frac{\partial p_x}{\partial y}\, dx. \tag{25}$$

Denote by $(c_c)_x$ and $(c_a)_x$ the concentrations of cations and anions, respectively, at a distance x from the interface. Then

$$p_x = \left\{ (c_c)_x + (c_a)_x \right\} RT = cRT \left(e^{-\frac{(\varphi + E_t y)F}{RT}} + e^{\frac{(\varphi + E_t y)F}{RT}} \right).$$

Integrating equation (24) between the limits x and ∞ we obtain

$$\frac{k}{8\pi}\left(\frac{\partial \varphi}{\partial x}\right)^2 = RTc\left\{ e^{-\frac{(\varphi + E_t y)F}{RT}} + e^{\frac{(\varphi + E) y_t F}{RT}} - 2 \right\} = p_x - p_\infty. \tag{26}$$

Equations (25), (24) and (26) yield:

$$(F_t)_x = -cF\left\{e^{-\frac{(\varphi+E_t y)F}{RT}} - e^{\frac{(\varphi+E_t y)F}{RT}}\right\}\left(\frac{\partial\varphi}{\partial y}\right) + \\ + cF\left\{e^{-\frac{(\varphi+E_t y)F}{RT}} - e^{\frac{(\varphi+E_t y)F}{RT}}\right\}\left(\frac{\partial\varphi}{\partial y} + E_t\right) = E_t\varepsilon_x. \qquad (27)$$

Thus, taking into account the osmotic pressure gradient, one not only obtains the same resultant ponderomotive force in the double layer of a metallic particle as in the case of a non-conducting particle, but also finds the same dependence on the distance x, as determined by the dependence of ε_x on x[18].

The difference between the two cases, just as in the case of a Helmholtz layer, resolves to the following: the force acting on the inner sheet of the double layer on the metal surface is equal to zero or, to be more exact, its point of application is displaced a distance of the order of the particle radius. Whether

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[18] In an unpolarized diffuse double layer the excess lateral pressure on an element of the surface layer of thickness dx, the integral of which over the entire surface layer gives the magnitude of the surface tension lowering, equals the extra osmotic pressure of the ions of the double layer $(p_x - p_\infty)\,dx$ plus the Maxwell pressure $\frac{k}{8\pi}\left(\frac{\partial\varphi}{\partial x}\right)^2 dx$, both these terms being equal. However, were we to obtain the force $(F_t)_x\,dx$ from the relation

$$(F_t)_x\,dx = -\frac{\partial}{\partial y}\left\{\frac{k}{8\pi}\left(\frac{\partial\varphi}{\partial x}\right)^2 + (p_x - p_\infty)\right\} dx, \qquad \text{(a)}$$

we should arrive at an erroneous result. This is due to the circumstance that the electrical part of the ponderomotive force in the double layer, expressed in terms of the components of the Maxwell stress tensor, should contain, besides the terms T_y^y the terms T_y^x which are absent in an unpolarized double layer. In this case, neglecting the term containing $(\partial\varphi/\partial y)^2$ in the expression for T_y^y, we obtain the following correct expression for the electrical part of the ponderomotive force:

$$\frac{\partial T_y^y}{\partial y}\,dx + \frac{\partial T_y^x}{\partial x}\,dx = \frac{\partial}{\partial y}\left\{-\frac{k}{8\pi}\left(\frac{\partial\varphi}{\partial x}\right)^2\right\} dx + \frac{\partial}{\partial x}\left\{\frac{k}{8\pi}\frac{\partial\varphi}{\partial x}\frac{\partial\varphi}{\partial y}\right\} dx = \\ = \frac{k}{4\pi}\frac{\partial^2\varphi}{\partial x^2}\frac{\partial\varphi}{\partial y}\,dx.$$

The quantity T_y^x vanishes at both boundaries of the double layer. This explains why integration of the inexact relation (a) leads to a correct result.

or not, equation (27) can be applied to a double layer of arbitrary structure, when specific adsorption forces are operative, remains as yet unclear, and we are limited in the most general case to the method of approach outlined above, which is based on the thermodynamic Lippman—Helmholtz equation. The terms $\frac{k}{4\pi}\frac{\partial^2\varphi}{\partial x^2}\frac{\partial\varphi}{\partial y}\,dx$ and $\frac{\partial p_x}{\partial y}\,dx$ in equation (25) are comparable in magnitude. Indeed,

$$\int_0^\infty \frac{k}{4\pi}\frac{\partial^2\varphi}{\partial x^2}\frac{\partial\varphi}{\partial y}\,dx = \frac{k}{4\pi}\left|\frac{\partial\varphi}{\partial x}\cdot\frac{\partial\varphi}{\partial y}\right|_0^\infty - \frac{k}{8\pi}\int_0^\infty \frac{\partial}{\partial y}\left(\frac{\partial\varphi}{\partial x}\right)^2 dx = -\int_0^\infty \frac{\partial p_x}{\partial y}\,dx,$$

and, according to equations (24) and (26),

$$\int_0^\infty \frac{k}{4\pi}\frac{\partial^2\varphi}{\partial x^2}\frac{\partial\varphi}{\partial y}\,dx = -\int_0^\infty \frac{\partial p_x}{\partial y}\,dx = -\frac{1}{2}E_t\cdot\varepsilon,$$

where ε, as formerly, is the charge of the inner sheet of the double layer. The ratio of the electrical and osmotic components of the ponderomotive force equals

$$\frac{k}{4\pi}\frac{\partial^2\varphi}{\partial x^2}\frac{\partial\varphi}{\partial y} : -\frac{\partial p_x}{\partial y} = -\left(\frac{\partial\varphi}{\partial y}\right) : \left(\frac{\partial\varphi}{\partial y} + E_t\right).$$

At comparatively large distances from the particle this ratio becomes infinite and the ponderomotive force is determined solely by the electrical component. At sufficiently small distances on the contrary, it is equal to zero, and the ponderomotive effect depends entirely on the osmotic term.

It remains now to discard the assumption that the metal—solution interface is impenetrable to the ions, and to consider the case of a partially polarizable spherical particle. We shall retain the assumption, however, that the distortion of the double layer induced by the current is so small that, in computing the forces from the potential distribution, we may consider he double layer as being in equilibrium, corresponding to the given potential difference. In addition we shall assume that the change in the potential difference $\Delta\varphi$ induced by the flow of current through the metal—solution interface is small compared with the quantity RT/F. Then, instead of the boundary condition for an ideally polarizable particle $(\partial\varphi/\partial r)_{r=a}=0$, where a is the radius of the particle plus its surrounding double layer (*i. e.* instead of the former quantity $a+d$) we have:

$$\varphi_{r=a}=jw=\varkappa\left(\frac{\partial\varphi}{\partial r}\right)_{r=a}\cdot w, \tag{28}$$

taking into consideration, as before, that $\varphi_{r=a}$ vanishes at $\theta=\pi/2$. Here j is the current density normal to the surface of the sphere, directed from the solution to the metal, and w is a constant depending on the nature of the polarization process. If the polarization is purely concentrational, then for the case of discharge and formation of a cation, $w=\frac{RT}{n_cFj_d}$, where n_c is the valency of the cation and j_d — the density of the limiting diffusion current. For chemical polarization $w=RT/nFj_0$, where n is a constant of the order of unity which depends on the mechanism of the reaction, and j_0 is the «exchange current» between the metal and the solution, which determines the rate of exchange between the two phases in the absence of polarization. In any case the quantity w characterizes the polarizability of the electrode, and if it is very large, condition (28) practically coincides with the condition $(\partial\varphi/\partial r)_{r=a}=0$ given above.

The solution of Laplace's equation under the boundary condition (28), when the field intensity E at large distances from the drop is parallel to the y-axis, has the form (for $r\gg a$):

$$\varphi=-E\cos\theta\left(r+\frac{\varkappa w-a}{2\varkappa w+a}\,\frac{a^3}{r^2}\right), \tag{29}$$

and for $r=a$:

$$\varphi=-\frac{3}{2}Ea\cos\theta\,\frac{1}{1+\frac{a}{2\varkappa w}}. \tag{29a}$$

A comparison of equations (29a) and (9a) shows that the ponderomotive forces are $1:\left(1+\frac{a}{2\varkappa w}\right)$ times less than for an ideally polarizable drop. The solution (29) is correct only if the quantity w does not itself depend on θ. In the case of concentration polarization, assuming that the stirring depends on the motions of the drops themselves, the quantity j_d, and therefore, w, depends on θ in a complicated manner, and an exact solution of the problem becomes impossible. In Section 4 we shall return to several peculiarities of this case.

We proceed to estimate the limiting value of the coefficient $k = 1 + \frac{a}{2\varkappa w}$, which determines the decrease in the electrocapillary effects due to incomplete polarizability of the drop. The maximum value of k corresponds to minimum w. Inasmuch as concentration polarization unfailingly accompanies every electrochemical process, minimum w should be observed in the presence of concentration polarization alone and in solutions which do not contain foreign electrolytes not participating in the reaction. In this case the concentration polarization is equal to the product of the ohmic potential drop in the Nernst diffusion layer[19] into the ratio of the valencies of anion and cation n_a/n_c and, therefore, with small values of this polarization:

$$w = \frac{\delta}{\varkappa} \frac{n_a}{n_c},$$

where δ is the thickness of the Nernst diffusion layer, and

$$k = 1 + \frac{a}{2\varkappa w} \sim \frac{a}{\frac{2n_a}{n_c}\delta} \sim \frac{a}{\delta}.$$

In regimes of stirring, that may be encountered when observing mercury drops, δ lies between 10^{-2} and 10^{-4} and k cannot exceed a few hundred. Thus, even under comparatively favourable conditions of polarization, the forces acting on a metallic particle are quite considerable. Below we give a somewhat more precise computation of k.

In deducing the relations of Section 3 we assumed that the distribution of the lines of current near the particle is not disturbed by its surface conductivity; *i. e.*, that the surface conductivity is small compared with the conductivity of a volume of the solution of linear dimensions corresponding to the dimensions of the particle. In the case of a solid particle this condition will be fulfilled if $\varepsilon c F a \ll 1$; since for not too small values of $\Delta\varphi$ we have $\varepsilon \sim 10^{-5}$ coul/cm^2, it follows, hence, that for a

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[19] B. Levich and A. Frumkin, J. Phys. Chem. (Russ.), **15**, 748 (1941); Acta Phys. Chim., **18**, 335 (1943).

$10^{-4}N$ solution $a \geqslant 10^{-2}$, while for a $10^{-5}N$ solution $a \geqslant 10^{-1}$. Thus, only in the case of sufficiently large particles is it permissible to neglect the correction for surface conductivity in dilute solutions. In the case of liquid particles it will be shown below that owing to the appearance of a large convection conductivity, this correction is of even greater importance.

4. The movement of metallic particles in an electric field

With a knowledge of the distribution of the forces acting on the surface of a metallic particle we can proceed to consider the problem of its motion in a solution under the influence of an impressed electric field. We shall not go into the strict hydrodynamical theory here, which was developed by B. Levich, leaving that to another paper (Part III), but shall limit ourselves to semi-quantitative dimensional estimates. As will appear from what follows, such estimates not only permit us to explain the physical nature of the motion but bring to relations which differ from the strict quantitative ones only by unessential numerical coefficients.

Let us begin with the simpler case of the motion of a solid metallic particle. As appeared in the preceding section, a correct evaluation of the polarizability of the double layer on the surface of a metallic particle brings to expression (14) or (26) for the ponderomotive force; this does not differ from the corresponding expression for the force on the double layer of a non-conducting particle. In the case of a metallic particle the point of application of the force acting on the inner sheet of the double layer is displaced a distance of the order of magnitude of the particle radius. As a result elastic strains are induced in the solid metallic particle which compensate the difference of the corresponding electrical stresses acting on the surface. However, the deformations thus brought about in solid particles whose linear dimensions in various directions differ but slightly[20], have no influence on the motion of the particle as a whole. The motion of a solid metallic particle in an electric field is, therefore, ordinary cataphoretic motion and may be described by the same relations as for a dielectric particle.

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[20] In the case of a thin metallic foil when the polarization conditions are suitably chosen, these strains can give rise to observable changes in form; this can be utilized to investigate electrocapillary phenomena on solid metals.

The case is quite different with liquid metal particles, *e. g.* mercury droplets in an electric field in a solution. The electric forces acting on the surface of a liquid particle cannot, of course, be compensated by mechanical strains and will, therefore, induce motion of the liquid inside the particle. The viscous strains arising as a result of such motion will play the part of the mechanical strains in a solid particle in compensating the electric forces.

Since adjacent layers in viscous fluids are completely carried along, the motion of the liquid inside the particle will be transmitted to the surrounding solution. As a result the particle will begin to move as a whole relatively to the distant layers of the external liquid. It was this motion of liquid metallic particles which Christiansen investigated.

From the viewpoint of the theory here exposed there is no fundamental difference between the electrocapillary motion of liquid metallic particles and the cataphoretic motion of solid metallic particles. In both cases the motion is induced by the same system of electric forces, the essential difference between the two types of motion lying merely in the different realization of these forces.

It should also be observed that the motion of the external liquid is composed, in general, of two motions: one due to the pull of the inner liquid, the other—to the cataphoretic motion of the mobile (not fixed to the mercury) sheet of the double layer. The latter component does not differ from ordinary cataphoresis, and inasmuch as its velocity is small compared with the velocities of electrocapillary motion, we shall neglect it in the sequel.

We now turn to a more detailed consideration of the electrocapillary motion of a mercury drop placed in an electric field (Fig. 2).

For the sake of definiteness, we shall consider, as above, that the drop carries a positive charge. To each square centimetre of its surface are applied a tangential force F_t and a normal force F_n (see equations (20) and (21)), which induce motion of the liquid inside the drop. It is clear from expressions (20) and (21) and Fig. 2 that the general picture of the motion is as follows. Under the influence of the force F_t which is directed towards increasing θ the surface layer of the liquid will move along the drop from right to left. Besides the tangential forces, electrical normal forces represented in Fig. 2, diminishing the capillary pressure, are also operative. The latter is, therefore, larger in the left-hand half of the drop, at values of θ close to π.

This difference in capillary pressures causes a motion of the liquid in the drop from left to right. As a result a system of eddy currents arises inside the drop, as depicted by the arrows in Fig. 2. Inasmuch as the layers of mercury moving along the surface of the drop will drag along the adjacent layers of solution, the external liquid will also be brought into motion as depicted by the arrows in Fig. 2, while the drop itself as a whole will obviously recoil from left to right along the applied field E.

A qualitatively similar theory was set forth in the work of Christiansen; however, up to the present, no attempts were made to study the phenomenon quantitatively, while even the qualitative conceptions developed by Christiansen contain some inaccuracies.

The velocity of electrocapillary motion can be estimated in order of magnitude by means of semi-quantitative dimensional considerations. To carry out such an estimate it is necessary to bear in mind that the motion of the mercury surface is accompanied by a transfer of ions in the outer sheet of the double layer. The electric current of convection thus arising tends to equalize the potential along the surface of the drop. There are thus two essentially different limiting regimes of flow: one, in which the convection current is so small that equalization of the potential can be neglected, and another, in which the convection current is so large that the potential along the drop is almost completely equalized.

It may be assumed that in the first regime the potential jump across the metal—solution interface depends on the angle according to equation (10), so that on each square centimetre of surface a tangential and a normal force given by formulae (20) and (21) are operative. These forces should be compensated by the viscous drag in the moving liquid.

If μ and μ' are the respective viscosities of the external (solution) and internal (mercury) liquids, U—the characteristic velocity of the liquid and a—the radius of the drop, then the viscous drag in the external and internal liquids will be, respectively, in order of magnitude $\frac{\mu U}{a}$ and $\frac{\mu' U}{a}$. Hence, we can write approximately:

$$\frac{\mu U}{a} + \frac{\mu' U}{a} \sim \varepsilon E.$$

The characteristic velocity of the liquid can be identified in order of magnitude with that of the recoil movement of the drop as a whole relative to the solution. Thus, in the case of the first regime of flow the velocity of electrocapillary motion of the drop is of the order of magnitude of

$$U \sim \frac{\varepsilon E a}{\mu + \mu'} \tag{30}$$

We see that the velocity U is proportional to the surface charge density on the drop and inversely proportional to the viscosities of the solution and the mercury.

In particular, if μ' tends to infinity, which corresponds to the transition to a solid particle, the velocity of the electrocapillary motion becomes zero. In reality, however, it goes over into the velocity of ordinary cataphoretic motion, which, as was pointed out above, was neglected from the very beginning.

According to equations (2a) and (30) in order of magnitude velocities of the electrocapillary and cataphoretic motions should be in the ratio of $a : d$, *i. e.* the velocity of motion of a mercury drop of the usual dimensions (of the order of 10^{-1}—10^{-2} cm) should be approximately one hundred thousand times as large as the velocity of a solid metallic particle.

Let us now consider the second regime of flow, when the change along the surface of the drop of the potential jump across the interface is brought to zero by the convection current of ions. In this case the potential of the solution near the drop is constant at all points and can be represented by the same expression as for an unpolarizable metallic particle:

$$\varphi = \varphi_0 + \left(a - \frac{a^3}{r}\right) E \cos\theta.$$

The density of the current flowing onto the drop being thereby

$$j_r = -\varkappa\left(\frac{\partial\varphi}{\partial r}\right)_{r=a} = -3\varkappa E\cos\theta.$$

In order that the potential jump at the drop—solution interface remain constant, it is necessary that the convection current of the ions of the outer sheet carried along the surface of the drop by the liquid be equal to this electric current. The convection current of the charges of the inner sheet is short-circuited by the conduction current flowing inside the mercury drop. Inasmuch as the electrical conductivity of the mercury is large compared with that of the solution, the potential difference which thereby sets in can be discarded. A schematic representation of the lines of current for such a regime of motion is given in Fig. 3.

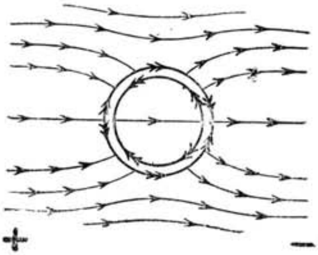

Fig. 3. Distribution of the lines of current taking into account the convective conductivity for an «ideally polarizable» drop of mercury. The single arrows denote the lines of conduction current in the solution and in the metal; the double arrows—the lines of convection current in the double layer. The convection current is of opposite direction in the outer and inner sheets since both sheets are moving in the same direction but carry charges of opposite sign.

If we denote by V_θ the tangential velocity of flow at the interface, then the convection current entering a spherical layer between θ and $\theta + d\theta$ will evidently be equal to $\varepsilon 2\pi a V_\theta \sin\theta$, the current emerging from the layer will be $\varepsilon 2\pi a\,[\sin\theta V_\theta]_{\theta + d\theta}$ and the difference between the two:

$$\varepsilon 2\pi a \frac{\partial}{\partial\theta}(V_\theta \sin\theta)\, d\theta.$$

Equating this quantity to the electric current $j_r 2\pi a \sin\theta\, d\theta$ flowing onto the ring between θ and $\theta + d\theta$, we find the following expression for the velocity of flow of the liquid along the surface of the drop in the second regime:

$$V_\theta = -\frac{3}{2}\,\frac{\varkappa E a \sin\theta}{\varepsilon}.$$

The velocity of motion of the drop as a whole will, therefore, be in order of magnitude

$$U = \frac{\varkappa E a}{\varepsilon}. \qquad (31)$$

We see that in the second regime of flow the velocity of the particle is inversely and not directly proportional to its surface charge density and, moreover, directly proportional to the electrical conductivity of the medium. A comparison of equations (31) and (4) shows that the second regime of flow exactly corresponds to the case (not realized with solid particles under usual conditions) when the bulk conductivity of the solution near the particle is negligible compared with the surface conductivity. In the general case we can obtain an approximate expression for U on the basis of the following consideration. The quantity of electricity, which is transferred in unit time from the right-hand half of the particle to the left-hand half owing to the motion of the surface, is equal in order of magnitude to $-V_{\pi/2}\,\varepsilon a$. The circuit of this convection current is closed by the conduction current in the solution. Since the electrolyte surrounding the drop presents a resistance of the order of $1/\varkappa a$ to the current flowing from one end of the drop to the other, the potential fall due to this conduction current in the solution adjacent to the drop will be equal in order of magnitude to $-V_{\pi/2}\,\varepsilon a/\varkappa a \sim -U\varepsilon/\varkappa$. It is of opposite sign to the potential fall near the drop due to the external field E, which in order of magnitude is equal to Ea (self-retarding effect). Hence instead of equation (30) we obtain

$$U \sim \frac{\varepsilon\left(Ea - \frac{U\varepsilon}{\varkappa}\right)}{\mu + \mu'}, \tag{31a}$$

therefore

$$U \sim \frac{\varepsilon E a}{\mu + \mu' + \frac{\varepsilon^2}{\varkappa}}.$$

The exact expression for the velocity of the drop in the general case, derived from the strict hydrodynamical theory (Part III) is

$$U = \frac{\varepsilon E a}{2\mu + 3\mu' + \frac{\varepsilon^2}{\varkappa}}. \tag{32}$$

Formula (32) shows that realization of the first or second regime of motion depends on the value of the dimensionless quantity $\frac{2\mu+3\mu'}{\varepsilon^2/\varkappa}$.

With $\frac{2\mu+3\mu'}{\varepsilon^2/\varkappa} \gg 1$, *i. e.* with a large viscosity and conductivity and small surface charge, the first regime of motion is realized, and the velocity of the drop equals

$$U=\frac{\varepsilon E a}{2\mu+3\mu'}.$$

In the contrary case $\frac{2\mu+3\mu'}{\varepsilon^2/\varkappa} \ll 1$, *i. e.* with small viscosity and conductivity and large charge, the second regime sets in and the velocity of the drop equals

$$U=\frac{\varkappa E a}{\varepsilon}.$$

It is convenient to introduce the mobility of the particle Z *i. e.* the ratio of the velocity U to the intensity of the external electric field E

$$Z=\frac{U}{E}=\frac{\varepsilon a}{2\mu+3\mu'+\frac{\varepsilon^2}{\varkappa}}. \tag{32a}$$

and the specific mobility of the surface z, *i. e.* the value of the mobility at unit radius:

$$z=\frac{\varepsilon}{2\mu+3\mu'+\frac{\varepsilon^2}{\varkappa}}. \tag{32b}$$

Formulae (32a) and (32b) reveal particularly clearly the dual rôle of the surface charge; on the one hand, it is the source of the motion of the drop; on the other hand, the cause of its self-retardation, an increase in the charge bringing about a damping of the motion.

At a charge density $\varepsilon=\varepsilon_{\max}$

$$\varepsilon_{\max}=\sqrt{\varkappa(2\mu+3\mu')},$$

the mobility attains a maximum value equal to

$$(z)_{\max}=\frac{1}{2}\sqrt{\frac{\varkappa}{2\mu+3\mu'}}.$$

The quantity $3ER$ is the maximum potential difference existing between two points on the particle surface in the absence of motion. Let us denote this difference by $\Delta\Phi_0$. Equation (32) may then be written in the following form:

$$U = \frac{1}{3} \frac{\varepsilon(\Delta\Phi_0)}{2\mu + 3\mu' + \frac{\varepsilon^2}{\varkappa}} = \frac{1}{3} Z_0 (\Delta\Phi_0). \tag{33}$$

It is interesting to observe that expression (32) for the velocity of a metallic drop is very similar in form to the corresponding expression (5) for a solid (metallic or dielectric) particle. If one ignores the difference in the numerical coefficients of μ, equation (32) can be obtained from (5) by substituting a for d in the coefficient before the quantities ε and $\varepsilon^2/\varkappa$.

This result may be interpreted in the following manner. In the case of a solid particle the viscous motion of the liquid due to the field should decay within the limits of the double layer, *i. e.* at distances of the order of d, whereas with a liquid metallic particle it should decay inside the particle itself, *i. e.* at distances of the order of the particle radius a. Hence in the latter case the viscous drag is less, and the corresponding velocity greater than in the former case in the ratio a/d. On passing over from a solid to a liquid particle the convective conductivity of the surface and, therefore, the retardation of the motion due to the electric field of the charges transported by the convection current on the particle surface also increase in the same ratio.

Let us consider now separately the mobility of mercury particles moving in a very viscous medium, and let the first regime of flow be in force. Then the following inequalities are satisfied:

$$\frac{\varepsilon^2}{\varkappa} \ll \mu \text{ and } \mu' \ll \mu.$$

For the velocity of the drop we obtain:

$$U = \frac{\varepsilon E a}{2\mu}.$$

Comparing this expression with (1) we see that the mobility of a mercury drop surrounded by a double layer equals $^3/_4$ the mobility which would be possessed by a solid particle in the same medium, carrying a free charge equal to the charge on the inner sheet of the double layer and $^1/_2$ the mobility of the same particle were it liquid. Inasmuch as the charge density in the double layer can be many times greater than the possible density of a free charge, mercury drops in a well conducting viscous medium possess relatively exceptionally high mobilities.

In the derivation of equation (32) two assumptions are made which limit its applicability. The first consists in a neglect of the ohmic surface conductivity of the drop compared with the bulk conductivity of the solution in computing the ponderomotive forces and the effect of self-retardation. As was shown at the end of Section 3, this is permissible only under the condition $\frac{s}{cFa} \ll 1$ which is, however, usually satisfied in experiments with macroscopical drops. According to the second, more essential assumption, in electrocapillary motions the surface tension at all points of the drop should depend only on the potential. This condition will not be fulfilled, for example, if the solution contains surface-active substances and if, due to the slowness of the adsorption or diffusion process, some time is needed for equilibrium to set in between the interface and the bulk of the solution. In this case, even with constant φ the interfacial tension will be greater on those parts of the drop where the mercury surface is expanded (the right-hand side in Fig. 2) and less where it is compressed (the left-hand side), this causes an additional drag on the motion of the surface and a decrease in its mobility[21].

Similar phenomena should take place even in the absence of substances specifically adsorbed, if only at the given potential equilibrium between the boundary layer and the bulk of the solution does not set in instantaneously. Thus, for example, if the surface of the mercury is charged negatively and the solution, in addition to univalent cations contains also polyvalent ones, there will be a relative excess of the latter in the surface layer, and, when the surface contracts, the adjoining layers of the solution become richer in polyvalent cations; as a result, although the potential is everywhere the same, the interfacial tension on various parts of the surface is different. It is

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[21] B. Levich, Contribution to the theory of surface phenomena. Moscow 1940 Publishers «Soviet Science».

obvious that the current through the solution cannot equalize such differences in composition, this being possible only by diffusion, *i. e.* by a comparatively slow process; hence the resulting retardation effects can be quite considerable.

The validity of the theory has also limitations due to increase in the velocity and potential gradient. It follows from the exact theory that if the variation in the interfacial tension over the surface is small compared with its initial value and the movement of the drop takes place in the region of small values of the Reynolds number, the drop will retain its spherical form unchanged during the motion. Numerical estimations, however, show that for large values of ε and sufficiently large drops the velocities U calculated by formula (32) are so great that the Reynolds number $\mathrm{Re} = Ua/\nu$ ($\nu = \mu/\rho$ — kinematic viscosity of the solution, ρ—its density) is by no means small compared to unity. In this case formula (30) is no longer valid and must be modified accordingly.

The motion of liquid bodies at values of the Reynolds number large compared with unity has been insufficiently studied in hydrodynamics both experimentally and theoretically. In such motion the drop loses its spherical form and becomes oval in shape with its obtuse end advancing. As to the forces acting on the drop, it follows from general considerations that under these conditions the viscous drag becomes small compared with the dynamical pressure and can be neglected.

The dynamical pressure per unit area of the drop surface may be expressed as follows:

$$P = \rho C_f U^2,$$

where C_f is the coefficient of resistance, which is an involved function of the Reynolds number. The form of this function in the case of a liquid drop is unknown. One may assume, however, that it does not differ very much from the similar function for a solid ovaloid and that with increase in Re the coefficient of resistance at first falls off rather steeply and then remains almost constant in a wide interval of Reynolds numbers.

For a very rough estimate of the velocity of the drop at values of $\mathrm{Re} \gg 1$ one may substitute the dynamic pressure for the viscous drag in formula (30) and write:

$$\rho C_f U^2 \sim \varepsilon E$$

$$U \sim \sqrt{\frac{\varepsilon E}{\rho C_f}} \tag{34}$$

Inasmuch as C_f is an unknown function here and can be considered constant only in the roughest approximation, formula (34) bears but a semi-quantitative character. It shows that at large values of Re the velocity of the drop should increase with the charge more slowly than follows from formula (32) and should depend but slightly on the viscosity of the solution and the mercury.

One is inclined to think that part of the changes in the form of the drop described by Christiansen were due to this very effect (simple estimates show that in these experiments the value of Re was considerably greater than unity) rather than to the variation of the interfacial tension over the surface of the drop, as Christiansen presumed.

This is also evident from the circumstance that if the change in the form of the drop were caused by the variation of the interfacial tension, the drop would take the form of an ovaloid with its narrow end pointing in the direction of motion, instead of in the opposite direction, as is actually the case. Indeed, the interfacial tension in the forward part of the drop is lowered, so that if the change in form were due to variation of the interfacial tension, this part should bulge out forming the narrow end of the drop.

Up to now we assumed in the calculations that the maximum variation of the potential of the drop is small compared with the initial potential jump.

$$\varphi_0 = \frac{\varepsilon}{C}$$

where C is the capacity of the double layer.

The maximum change of the potential jump in the double layer (Part III) is

$$\frac{(2\mu + 3\mu')}{2\mu + 3\mu' + \frac{\varepsilon^2}{\varkappa}} \cdot \frac{3Ea}{2}$$

Hence for the theory to be valid the inequality

$$\frac{2\mu+3\mu'}{2\mu+3\mu'+\frac{\varepsilon^2}{\varkappa}}\cdot Ea \ll \frac{\varepsilon}{C} \tag{35}$$

must be satisfied. This will always be so if $Ea \ll \varphi_0$.

If the inequality (35) is not satisfied, we may no longer neglect the variation of the charge density over the surface of the drop. In fact, this variation may be so great, that one side of the drop may be charged positively, the other negatively. In such a case a motion of the fluid described above but of opposite direction should arise on both ends of the drop. The resulting velocity of the drop should obviously fall off sharply thereby, and it becomes possible for the drop to break up, as Christiansen actually observed.

Let us now consider the case of a partially polarizable drop. Since we assume that the change of the potential jump at the metal—solution interface upon passage of the current is small, then if the drop is to be incompletely polarizable, *i. e.* if ions are to be neutralized and to form on its surface, an interchange of ions between the metal and the solution must also occur before the current is applied, as *e. g.* in the case of a mercury drop in a solution containing $Hg_2^{\cdot\cdot}$ ions, or a drop of zinc amalgam in a solution containing $Zn^{\cdot\cdot}$ ions.

In the case of a partially polarizable drop, as it was seen in the preceding section, the influence of the current passing through the drop reduces, according to equation (28a), the ponderomotive forces in the ratio of $1:\left(1+\frac{a}{2\varkappa w}\right)$. This refers to both the forces depending on the external field and those arising from the effect af self-retardation. Formula (32a) should, therefore, be written in the form

$$U=\frac{\varepsilon Ea\left(1+\frac{a}{2\varkappa w}\right)^{-1}}{2\mu+3\mu'+\frac{\varepsilon^2}{\varkappa}\left(1+\frac{a}{2\varkappa w}\right)^{-1}}=\frac{\varepsilon Ea}{(2\mu+3\mu')\left(1+\frac{a}{2\varkappa w}\right)+\frac{\varepsilon^2}{\varkappa}}\,. \tag{36}$$

Since, according to equation (29a), for an incompletely polarizable drop

$$\Delta\Phi_0=3Ea\left(1+\frac{a}{2\varkappa\omega}\right)^{-1},$$

equation (33) must be replaced in this case by the following:

$$U = \frac{1}{3} \frac{\varepsilon(\Delta\Phi_0)}{2\mu + 3\mu' + \frac{\varepsilon^2}{\varkappa}\left(1 + \frac{a}{2\varkappa\varpi}\right)^{-1}} . \tag{36a}$$

According to equation (36), which will be derived more strictly in Part III, with decreasing ϖ the velocity of the drop diminishes. The influence of the incomplete polarizability disappears if ϖ is sufficiently large compared with $\alpha/\varkappa$ and if the drop is in the second regime of motion. Indeed, if the external field is completely neutralized by the convection current due to the motion of the double layer, then the possibility of a current passing through the drop will not affect the velocity. However, as was shown in Section III, the derivation of equation (28a) implies that ϖ is independent of θ.

In the case of a moving drop, whose motion determines the regime of stirring, this condition is not fulfilled.

Let us consider qualitatively the phenomena which should be observed in this case for a positively charged drop (Fig. 2), *e. g.* a drop of mercury in a solution of a mercury salt. As the current flows through the drop, mercury ions are formed on the right-hand side of the surface increasing the ion concentration in the solution. On the left-hand side of the drop, on the contrary, ions are discharged and their concentration in the solution is correspondingly diminished. The changes in concentration which thus take place are, however, different in magnitude. Owing to the electrocapillary motions, a current of the fresh solution of the initial concentration flows to the right-hand side of the drop, whence, after becoming enriched, it streams on to the left-hand side. Here the excess ions are deposited on the mercury, so that the solution which flows away from the drop in the direction of negative y has on the average recovered the initial value of the concentration. Since during the time of flow the excess mercury ions will diffuse some distance from the surface of the drop into the solution, the layer of liquid adjacent to the left-hand side of the drop will have a concentration slightly lower than the original value while at a great distance the concentration of the solution will remain enhanced for some time. At a sufficiently large distance from the drop all these differences should disappear and at all points in the solution the concentration should return to its initial value. With such a distribution of concentration it is evident that the change in the concentration compared with the initial value, and hence the variation of the potential, are greater near the right-hand side of the drop than near the left-hand side. In other words, as was shown above, the quantity w depends on the angle θ and falls off as θ varies from 0 to π. Under these conditions the current should also cause a variation in the average value of the potential jump in the surface layer in such a direction as to bring about an increase in the positive charge of the drop.

If the drop is negatively charged, the whole picture is reversed. The liquid flows relative to the drop from left to right, and the ions are deposited out of a solution with the initial concentration of metallic ions. The depleted solution flows to the right-hand part of the drop, where its concentration is restored to the initial value. Under these conditions the magnitude of the change in the potential will be greater on the left-hand side of the drop than on the right-hand side, and the average value of the potential of the drop will be shifted in the sense of increasing negative charge of the metal surface.

Such an intricate dependence of w on θ prevents an exact computation of the influence of incomplete polarizability on the velocity of motion. An approximate estimate may be given by making use of equation (36) with an average value of w. Such a value may be obtained from the expression for the density of the limiting diffusion current j_d and the relation $w = RT/n_M F j_d$. B. Levich (unpublished data) found that the average value of the density of the limiting diffusion current in the case of a liquid drop is

$$\bar{j}_d = \frac{J_d}{4\pi a^2} = 0.85 \left(\frac{UD}{a}\right)^{1/2} n_M F c_M, \tag{37}$$

and in the case of a solid drop

$$\bar{j}_d = \frac{J_d}{4\pi a^2} = 1.1 \left(\frac{UD^2}{a^2}\right)^{1/3} n_M F c_M. \tag{38}$$

Here J_d denotes the total diffusion current onto the drop, n_M and c_M — respectively the valency and initial concentration (in gram-equivalent per cm^3) of ions of the drop metal.

As an example let us determine the magnitude of the coefficient $k = 1 + \frac{a}{2\varkappa w}$ with $a = 10^{-2}$, in the case of the deviation in an electric field of a mercury drop, falling under the influence of gravity in a solution containing a neutral electrolyte of concentration c and mercury ions of concentration c_M. It is assumed that the hydrodynamic conditions of motion of a liquid drop are satisfied $\left(\frac{\varepsilon^2}{\varkappa(2\mu + 3\mu')} \ll 1\right)$. Since $U \sim 30$ cm/sec. $D \sim 0.8 \cdot 10^{-5}$, $\varkappa \sim 1.2 \cdot 10^2\, c$, $n_M = 2$,

$$\frac{a}{2\varkappa w} = \frac{0.85\, U^{1/2} D^{1/2} a^{1/2} 2 F c_M}{2\varkappa \frac{RT}{F n_M}} \sim 10^2 \frac{c_M}{c}\,. \tag{39}$$

Thus the quantity $k = 1 + \frac{a}{2\varkappa w}$, which can be called the coefficient of depolarization, depends on the ratio of the concentration of the ions of the metal of the drop to the overall concentration of the solution. For $\frac{c_M}{c} \sim 10^{-2}$ this coefficient already differs noticeably from unity, and in the case $c_M = c$, *i. e.* for a mercury drop in a solution containing only a mercury salt, the deviation of the falling drop in an electric field is approximately one hundred times less than in the case of an ideally polarizable drop. It is essential to point out that contrary to statements encountered in the literature, the incomplete polarizability of a drop always makes its mobility less than that of an ideally polarizable drop.

The relations which we have deduced for the mobility of drops in an electric field could not be verified on the experimental material available in the literature. Christiansen, who determined quantitatively the deviation of falling drops, did not make simultaneous observations on the time of fall. The dimensions of the drops in his experiments were so considerable ($a = 5 \times 10^{-2}$) that it is impossible to attempt even an approximate estimate of their rates of fall in water by Stokes' formula.

It should be noted that in agreement with equation (31) the magnitude of the deviations in dilute solutions did not depend on the field E, but on the density of the current flowing through the solution. In this institute experiments are being carried out at the present moment by I. Bagotskaya on determining the mobility of mercury ions in water—glycerine solutions of electrolytes. The results obtained so far agree in order of magnitude with the theory here developed.

The mobility of the drops calculated by equation (32a) falls off with diminishing radius and for $a=10^{-4}$ cm (which corresponds to the particle dimensions in the mercury sols investigated by Bull and Söllner[5]), at 10^{-4} normal concentration, $\varkappa\sim10^{-5}$, $\varepsilon\sim2\times10^{-6}$ it should equal $\sim 5\times10^{-4}$ cm/sec. per V/cm., *i. e.* should approach the usual electrokinetic mobilities. However, a consideration of the experimental data in this paper, in particular, the appearance of negative values of the charge in the presence of capillary-active anions leads us to the conclusion that the velocity of the particles in sols is not determined by the total charge, but rather by the effective electrokinetic charge. This is incompatible with equation (32a), at any rate as long as the dimensions of the particle exceed considerably the thickness of the double layer. We are forced to the assumption that the surface of the mercury in the sols investigated had adsorbed impurities from the solution or become covered by a film of insoluble mercury salts and, hence, lost its complete mobility, as a result of which the drops of mercury in the sol behaved like solid particles. The electrokinetic properties of mercury sols deserve new investigation by improved experimental methods.

Summary

1. A quantitative theory of the action of an external electric field has been given for the cases of non-conducting particles, ideally polarizable and incompletely polarizable metallic particles.

It has been shown that in the case of a metallic particle the points of application of the forces acting on the charges of opposite sign are displaced relative to one another a distance of the order of the particle radius rather than the thickness of the double layer, as in the case of a non-conducting particle.

2. The mechanism of the electrokinetic motions of solid nonconducting and conducting particles is compared with the electrocapillary motions of metallic drops, and the theory of electrocapillary motions is given for the case of an ideally polarizable drop. It is shown that two regimes of electrocapillary motions exist. In one of them the velocity of motion of an ideally polarizable particle differs only by a numerical coefficient of the order of unity from the velocity of a particle carrying a free charge equal to the total charge of the inner sheet of the double layer on the surface of the drop. In the other, the convection current due to the motion of the particle surface almost completely neutralizes the external electric field, the velocity of motion of the particle is inversely proportional to its charge density. The conditions (low conductivity, low viscosity of the medium, large value of the charge) favouring the transition from the first regime to the second have been determined. It is shown that incomplete polarizability of the drop decreases its mobility.

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