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A Contribution to the Theory of Electric Endosmosis and a Few Related Phenomena

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§1. The inspiration for this study was consideration of the stability of turbid media and colloidal solutions. The problem was to check the reliability of the theory, supported by a few authors[1] , saying that sedimentation of particles in such media is prevented by the same electric forces that are responsible for the phenomenon of electric endosmosis and diaphragm currents. The first step was to extend the theory of these phenomena, provided by Helmholtz[2]. for the particular case of a liquid in a vessel of the shape of Poiseuille's tube.

The proposed generalization of the Helmholtz theory is by itself interesting, in view of the fact that the earlier experiments reported by Wiedemann and Quincke already referred to the area extending beyond the range to which the simple Helmholtz calculations can be applied.

It will be also interesting to compare the Helmholtz theory with the competing theory proposed by Lamb[3], based on somewhat different and simplified assumptions. When applied to liquids in Poiseulle's tubes these two theories give the same results, but it is expected that a difference that would permit discrimination between them will appear in a general case. However, our final results did not answer

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[*] See: this volume p. 177, item [21a] [ed. note].

[1] See: Hardy, *Proc. Roy. Soc.* **66**, p. 123, 1900

[2] *Wied. Ann.* **7**, p. 337, 1897; Ges. Abhanding. I, p. 855

[3] *Philos. Mag.* **25**, p. 52, 1888; this theory has been omitted in the brief description (which is quite good) of the phenomena considered here, in Winkelman, *Handb. III.* 1, p.493; I have come across it only after obtaining the results presented here, the analogy of my results is full despite differences in assumptions and methods.

which of the theories was correct as these two theories proved fully analogous and, from the mathematical point of view, the Lamb theory could be treated as a specific case of our calculations.

The considerations that are the main subject of this paper will be supplemented with a few comments on the question mentioned at the beginning and on some other phenomena that are related to this theory.

§2. Electric endosmosis is a long-known phenomenon, studied in detail by Wiedemann and Fround[4] in which electric current flowing through a diaphragm or narrow tubes or slits makes the liquid flow in one or the other direction[5]. If the vessel with the liquid is closed, so that the flow is stopped, a pressure difference appears, an increase near the cathode and a decrease near the anode, defined as the electroosmotic pressure.

The reverse phenomenon, known as the diaphragm current, takes place when a difference in potential (or an electric current) is generated as a result of the liquid flow through a diaphragm (small tubes or slits) upon application of external pressure. Quincke[6] explained these phenomena in terms of mutual interaction between the moving liquid and the double electric layers on the vessel walls.

In the first case, the positively charged part of the double layer, localized in the liquid, is set in motion by the external electric field and draws some liquid in the same direction, in the reverse case, the mechanical motion of this layer (induced by pressure) generates convective electrical currents.

The calculations presented by Helmholtz for these phenomena taking place in narrow tubes of regular circular cross-section for which the Poiseuille law hold, are indeed in agreement with the measurements performed by Quincke and Dorn[7], in respect to dependence on the size of tubes, pressure (potential) differences and the liquid conductivity.

This agreement is, however, closely related to the validity of the Poiseuille law, as the behavior of wider tubes, used by e.g. Clark and Edlund[8] to which this law cannot be applied, is completely different. In view of the above, it seems to me even more risky to apply ‘a priori’ the same calculations to the clay diaphragms used by Wiedemann and Freund, which were treated by Helmholtz as a set of Poiseuille

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[4] Wiendemann, *Pogg. Ann.* **87**. p, 321. 1852; Freud, *Wied. Ann.* **7**, p. 53, 1879.

[5] This direction is the same for water and electrolytes, while the opposite for some other substances, e.g. for terpentine in contact with sulfur.

[6] *Pogg. Ann.* **113**, p. 513, 1861.

[7] Quincke, *Pogg. Ann.* **107**, p. 1, 1859; **110**, p. 38, 1860; **113**, p. 513, 1861. Dorn, *Wied. Ann.* **9**, p. 513, 1880; **10**, p. 46, 1880.

[8] Clark, *Wied. Ann.* **2**, p. 335, 1877; Edlund, *Wied. Ann.* **1**, p. 184, 1877.

tubes[9]. The structure of clay is rather more similar to the arrangement of pellets, the clay pores are irregular in shape so they do not resemble Poiseuille tubes. Even more in contrast to Poiseuille tubes are the diaphragms used in the Quincke experiments, he used diaphragms of sand, sulfur powder, shellac, ivory fillings, a few times folded silk fabric and other materials.

The 'a priori' use of Helmholtz calculations for such materials seems fully unjustified. A generalization of the Helmholtz theory, which proves necessary, can be made as shown below.

We begin with electric endosmosis.

§3. As long as a liquid is at rest in the normal state, the electric potential φ, corresponding to the activity of surface double layers will take a constant value φ_l inside the liquid, φ_c inside the wall, in the surface layers (of δ in thickness) it will change along the normal, while in the tangential direction it will be constant. The charge density

$$\varepsilon = -\frac{1}{4\pi}\frac{\partial^2\varphi}{\partial n^2},$$

positive from the side of water and negative on the side of the solid, will thus take values of the order of $\frac{1}{\delta^2}$.

Application of an external electric field, defined by the potential Φ, the total potential will take the value of

$$U = \varphi + \Phi.$$

As the mechanical force [following from the above] drives a tangential motion, another component V should be added to take into account the deformation of double layers. However, we will restrict our considerations to motions so slow that the interaction of this secondary phenomenon could be neglected with respect to the contributions of φ_l and Φ.

As we consider "slow" motions, we can neglect the effect of the liquid inertia. Taking into account the mechanical forces $\varepsilon\Delta U$, the hydrodynamic equations will become:

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[9] The fact that the amount of the liquid flowing through is proportional to pressure does not make any proof; it only proves that the motion is „slow", i.e. it satisfies the equation:

$$\frac{\partial p}{\partial x} = -\mu\Delta^2 u \quad \text{etc.}$$

$$\begin{cases} \dfrac{\partial p}{\partial x} = \mu\Delta^2 u - \varepsilon\dfrac{\partial U}{\partial x} \\ \dfrac{\partial p}{\partial y} = \mu\Delta^2 v - \varepsilon\dfrac{\partial U}{\partial y} \\ \dfrac{\partial p}{\partial z} = \mu\Delta^2 w - \varepsilon\dfrac{\partial U}{\partial z}. \end{cases} \tag{1}$$

The components $\varepsilon\frac{\partial\Phi}{\partial x}$ etc. cause movement of the liquid, while the components $\varepsilon\frac{\partial\varphi}{\partial x}$ (present also in the state of equilibrium) generate only pressure which is uniform in each single layer.

To eliminate the components of mechanical forces that can be neglected, we introduce the quantity P which will be described by the following equation, in which the distance along the normal to the layer is denoted as ζ,

$$P = p - \int_{\zeta}^{\delta} \varepsilon\frac{\partial\varphi}{\partial\zeta}d\zeta = p + \frac{1}{8\pi}\left(\frac{\partial\varphi}{\partial\zeta}\right)^2\Big|_{\zeta}^{\delta}. \tag{2}$$

Thus, we will have

$$\frac{\partial P}{\partial\zeta} = \frac{\partial p}{\partial\zeta} + \varepsilon\frac{\partial\varphi}{\partial\zeta}. \tag{3}$$

On the other hand, assuming ξ and η in the tangential directions, e.g. in the direction of the curvature, we have

$$\frac{\partial P}{\partial\xi} = \frac{\partial p}{\partial\xi} + \frac{1}{4\pi}\frac{\partial\varphi}{\partial\zeta}\frac{\partial^2\varphi}{\partial\xi\partial\zeta},$$

which can be simplified further as $\partial\varphi/\partial\xi$ is always zero because of the layer's uniformity, so:

$$\frac{\partial P}{\partial\xi} = \frac{\partial p}{\partial\xi}; \qquad \frac{\partial P}{\partial\eta} = \frac{\partial p}{\partial\eta}. \tag{4}$$

Applying equations (1) to the above defined directions ξ, η and ζ, we get the simplified equations

$$\begin{cases} \dfrac{\partial P}{\partial\xi} = \mu\Delta^2 v_\xi - \varepsilon\dfrac{\partial\Phi}{\partial\xi} \\ \dfrac{\partial P}{\partial\eta} = \mu\Delta^2 v_\eta - \varepsilon\dfrac{\partial\Phi}{\partial\eta} \\ \dfrac{\partial P}{\partial\zeta} = \mu\Delta^2 v_\zeta - \varepsilon\dfrac{\partial\Phi}{\partial\zeta}. \end{cases} \tag{5}$$

In order to disclose the significance of the quantity P, we differentiate eq. (5) with respect to ξ, η and ζ, which – taking into account the condition of incompressibility and equation $\Delta^2\Phi = 0$ – brings:

$$\Delta^2 P = -\frac{\partial \varepsilon}{\partial \zeta}\frac{\partial \Phi}{\partial \zeta}, \tag{6}$$

while from eq. (1) in a similar way we can get:

$$\Delta^2 p = -\frac{\partial \varepsilon}{\partial \zeta}\left(\frac{\partial \varphi}{\partial \zeta} + \frac{\partial \Phi}{\partial \zeta}\right). \tag{7}$$

As the term $\partial\Phi/\partial\zeta$ vanishes on the surface of insulating walls because electric current must flow in tangential direction, within the layer this derivative will take a small value of the order of δ. Therefore, the conclusion is that outside the layer P is identical to the hydraulic pressure p, but upon the abrupt change in p of the order of $1/\delta^2$ within the layer, induced by electrostatic pressure, P in the first approximation disappears from this relation. Only the terms of lower order remain and they can generate only finite differences in P at different points in the layer.

§4. Let's note now that the tangential forces $\partial\Phi/\partial\xi$ and $\partial\Phi/\partial\eta$ in eq. (5) are finite, so the terms on the right side will take values of the order of $1/\delta^2$, while the terms on the left side will be finite.

Multiplying the equations by ζ and taking integral between the limits 0 and δ, we will get:

$$\int_0^{\delta} \frac{\partial P}{\partial \xi}\zeta d\zeta = 0; \qquad \int_0^{\delta} \frac{\partial P}{\partial \xi}\eta d\zeta = 0, \tag{8}$$

while the right side of these equations will be finite.

As far as the Δ^2 operations are concerned, it should be remembered that they refer to the constant direction of the axis, so in general we cannot assume that

$$\Delta^2 = \frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2} + \frac{\partial^2}{\partial \zeta^2},$$

because the directions ξ, η and ζ are variable. Anyway, the term taking the highest value, which we should only be concerned with as the other terms vanish as a result of integration, is $\partial^2 v_\xi/\partial\zeta^2$ or $\partial^2 v_\eta/\partial\zeta^2$.

As $\partial v_\xi/\partial\zeta$ is finite outside the layer and v_ξ disappears at the surface $\zeta = 0$, by partial integration we get:

$$\int_0^{\delta} \frac{\partial^2 v_\xi}{\partial \zeta^2}\zeta d\zeta = \zeta\frac{\partial v_\xi}{\partial \zeta}\bigg|_0^{\delta} - \int_0^{\delta} \frac{\partial v_\xi}{\partial \zeta}d\zeta = -v_\xi\bigg|_0^{\delta}. \tag{9}$$

In the integral

$$\int_0^{\delta} \varepsilon \frac{\partial \Phi}{\partial \xi} \zeta d\zeta$$

the term $\partial\Phi/\partial\xi$ can be assumed as constant within δ, while the remaining integral can be calculated in a similar way

$$\int_0^{\delta} \varepsilon \zeta d\zeta = -\frac{1}{4\pi} \int_0^{\delta} \frac{\partial^2 \varphi}{\partial \zeta^2} \zeta d\zeta = \frac{(\varphi_l - \varphi_a)}{4\pi}. \tag{10}$$

Therefore, the final result is that the tangential velocity at the infinitesimal distance δ from the vessel walls is finite and equal to

$$v_{\xi} = -\frac{(\varphi_l - \varphi_a)}{4\pi\mu} \frac{\partial \Phi}{\partial \xi}, \qquad v_{\eta} = -\frac{(\varphi_l - \varphi_a)}{4\pi\mu} \frac{\partial \Phi}{\partial \eta}. \tag{11}$$

§5. The lines of current near the walls must be approximately parallel to them, so the normal velocities cannot be higher than a value of the order of δ because the flux flowing through the layer of thickness δ in the tangential direction must be the same as the flux flowing out through a finite element of the layer surface in the normal direction.

In order to get the velocity and distribution of pressure P in the layer we should use the continuity equation and eqs. (5, 3), but it would not be necessary as for further considerations it is enough to know that the normal velocity takes values of the order of δ, so it can be neglected in comparison to the other terms.

Now it is easy to calculate the distribution of velocities in the bulk of the liquid, as it is defined by the equations:

$$\frac{\partial p}{\partial x} = \mu \Delta^2 u; \qquad \frac{\partial p}{\partial y} = \mu \Delta^2 v; \qquad \frac{\partial p}{\partial z} = \mu \Delta^2 w, \tag{12}$$

and the boundary conditions corresponding to the relations given below, neglecting the infinitesimally small differences:

$$v_{\xi} = -\frac{(\varphi_l - \varphi_a)}{4\pi\mu} \frac{\partial \Phi}{\partial \xi}, \qquad v_{\eta} = -\frac{(\varphi_l - \varphi_a)}{4\pi\mu} \frac{\partial \Phi}{\partial \eta}; \qquad v_{\zeta} = 0.$$

The above finding implies the solution

$$\begin{cases} u = -\dfrac{(\varphi_l - \varphi_a)}{4\pi\mu} \dfrac{\partial \Phi}{\partial x}; \quad v = -\dfrac{(\varphi_l - \varphi_a)}{4\pi\mu} \dfrac{\partial \Phi}{\partial y}; \\ w = -\dfrac{(\varphi_l - \varphi_a)}{4\pi\mu} \dfrac{\partial \Phi}{\partial z}; \quad p = \text{const.} \end{cases} \tag{13}$$

That is to say that the mechanical currents will be proportional to the electrical currents and in the same direction, if $(\varphi_l - \varphi_a)$ is positive.

However, a reservation must be made regarding the electrodes through which the electric potential is applied, as the above calculation assuming the existence of (isolating) insulating walls cannot be applied to them. At the electrodes our calculations would lead to absurdity because the amount $(\varphi_l - \varphi_a)I/4\pi\mu\lambda$ of the liquid (where I is the total electric current and λ is the conductivity) would have to flow through the electrode surface.

We will circumvent this difficulty by imposing on this motion a distribution corresponding to a source of the size $(\varphi_l - \varphi_a)I/4\pi\mu\lambda$ in the cathode and the outflow of the same amount through the anode, at the usual assumption of the liquid adhesion to the vessel walls[10]. The velocities and pressures following from the above, taking into account the usual rules of hydromechanics of viscous liquids, will be denoted as u_0, v_0, w_0 and p_0. Consequently, the motion described by the following equations

$$\begin{cases} u = u_0 - \dfrac{(\varphi_l - \varphi_a)}{4\pi\mu}\dfrac{\partial\Phi}{\partial x}; \quad v = v_0 - \dfrac{(\varphi_l - \varphi_a)}{4\pi\mu}\dfrac{\partial\Phi}{\partial y}; \\ w = w_0 - \dfrac{(\varphi_l - \varphi_a)}{4\pi\mu}\dfrac{\partial\Phi}{\partial z}; \quad p = p_0, \end{cases} \tag{14}$$

will satisfy all the conditions of the problem, the fundamental equations, boundary conditions for insulating walls, condition of stability at the electrode surface, so it will be the solution to our problem.

§6. We introduce now the conditions similar to the actual examples that we are interested in, we assume that the entire vessel is made of two chambers with the electrodes linked through a narrow pipe that exerts significant resistance to the flow of the liquid.

We shall distinguish two cases.

α) The liquid can freely flow into the chambers from outside or leave them so that no difference in pressure can appear between them,

β) The chambers are closed so that the liquid can circulate only within the vessel.

In the first situation we deal with the phenomenon of electric endosmosis, the

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[10] It could be supposed that on the electrodes' surfaces a tangential motion could also be generated, similarly as on the isolating walls. In any case a modification of motion originating from this fact will have to be restricted to the immediate surrounding of the electrode. Moreover, it should be noted that the surface of well-conducting electrode will be equipotential so there is no reason why tangential motion should appear.

pressure p_0 will be infinitesimally small, just as the influence of u_0, v_0 and w_0 in the narrow pipe, so that we have to consider only the velocities defined by eq. (13).

The total amount of liquid flowing in the direction of the electric current will be $\mathcal{M} = \int v_n ds$, where the integral refers to the equipotential cross-section $\Phi =$ const in the linking pipe, so

$$\mathcal{M} = \frac{(\varphi_l - \varphi_a)}{4\pi\mu} \int \frac{\partial \Phi}{\partial n} ds = \frac{(\varphi_l - \varphi_a)}{4\pi\mu} I\sigma, \tag{15}$$

where σ is the specific resistance of the liquid.

In the second case, as follows from eq. (14), to the above described current must be superimposed a current of velocity (u_0, v_0, w_0) flowing in the opposite direction so that the total flow must be zero:

$$0 = \frac{(\varphi_l - \varphi_a)}{4\pi\mu} I\sigma + \int v_{\mathrm{no}} ds.$$

On the other hand, the flow of the amount $\int v_{\mathrm{no}}$ of viscous liquid through the connecting pipe implies a difference in pressure p_0, proportional to this amount of liquid and to its viscosity coefficient, which means that the pressure near the cathode will be higher than that near the anode and the difference is the electroosmotic pressure:

$$p_1 - p_2 = -C\mu \int v_{\mathrm{no}} ds = C \frac{(\varphi_l - \varphi_a)}{4\pi} I\sigma. \tag{16}$$

§7. Let's note that eq. (15) is identical with that proved by Helmholtz for the special case of Poiseuille tubes, moreover, that his formula for the electroosmotic pressure

$$P = p_2 - p_1 = \frac{(\varphi_l - \varphi_a)}{4\pi} \frac{8(V_2 - V_1)}{R^2}. \tag{17}$$

Is a special case of our general result (16) as according to the Poiseuille law

$$C = \frac{8l}{R^4 \pi},$$

while according to Ohm's law

$$I\sigma = \frac{R^2 \pi (V_2 - V_1)}{l}.$$

These results are fully consistent with the experiments of Wiedemann and Freund. As far as the electric endosmosis is concerned, these results have proved proportionality of the liquid current to the electric current, irrespective of the diaphragm thickness and area; also the dependence on σ has been approximately verified for solutions of different concentrations.

Exact verification cannot be expected as $(\varphi_l - \varphi_a)$ also depends on the solution concentration. On the other hand, according to Wiedemann, the electroosmotic pressure is defined by the equation $I\sigma d/\Omega$, where d is the thickness, Ω is the diaphragm area, which also follows from eq. (16) as the constant C defined in this equation must be proportional to d/Ω for diaphragms of a uniform structure.

§8. Besides the above-mentioned phenomena, our theory can be applied to other known phenomena of transportation of fine particles caused by electric current[11].

Let's consider for instance a ball made of insulating solid submerged in liquid of infinite mass and subjected to a uniform electric field. Assuming the field direction as the axis of a polar system, we will get the following distribution of external potential Φ:

$$\Phi = -cx\left(1 + \frac{a^3}{2r^3}\right) = -c\cos\theta\left[r + \frac{a^3}{2r^3}\right]. \tag{18}$$

If the ball was fixed in space, the potential would cause the liquid movement in the direction of the field lines:

$$\left.\begin{aligned} u &= \frac{\partial}{\partial x} \\ v &= \frac{\partial}{\partial y} \\ w &= \frac{\partial}{\partial z} \end{aligned}\right\} \left[\frac{(\varphi_l - \varphi_a)}{4\pi\mu} cx\left(1 + \frac{a^3}{2r^3}\right)\right],$$

which at a greater distance [from the ball] would cause a movement of a constant velocity

$$u = \frac{(\varphi_l - \varphi_a)}{4\pi\mu} c. \tag{19}$$

However, if the ball is not fixed and can move in immovable liquid, as a result of the field activity the ball will move at the above velocity $(\varphi_l - \varphi_a)c/4\pi\mu$ (independent of the ball size) from the cathode to the anode. To get an idea of quantitative relations let's assume e.g.

$$(\varphi_l - \varphi_a) = 2\,\text{Volt}, \qquad \mu = 0.018, \qquad c = 1\,\frac{\text{Volt}}{\text{cm}};$$

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[11] See: Quincke, *Pogg. Ann.* **113**, p. 546, 1861.

then we will get

$$u = 0.000093\,\frac{\mathrm{cm}}{\mathrm{sec}}.$$

This velocity is of the same order as that of ions in electrolysis, which is surprising and could be used for further, although rather risky, speculations.

The measurements reported by Quincke show the proportionality of velocity to electromotive force, but no suitable data are given to make an exact comparison with experiment.

All the substances studied by Quincke moved in water towards the anode, while in turpentine oil usually in the reverse direction, so in the latter medium the potential difference $\varphi_l - \varphi_a$ must be negative. In narrow tubes a peculiar phenomenon was observed: if the current intensity in water was weak, the particles in direct neighborhood of the walls moved towards the cathode, while if the current intensity was higher, they moved towards the anode, like all other particles.

The first fact can be easily understood if we realize that in narrow tubes the motion of particles is superimposed by the liquid current (see §6, β) which is directed towards the cathode near the walls and towards the anode in the center of the tube. At the same time a rotation must take place, indeed noted by Quincke. However, our calculations do not explain the reverse of the direction of motion upon greater electric current, neither does the explanation by Quincke seem to be justifiable. In my opinion the reasons are some secondary factors, neglected in our theory, or some other phenomena related to rotation of poorly conducting solid bodies in an electric field.[12]

Recently, many observations of electric transportation of small particles, although usually only qualitative, have been made in investigation of colloidal solutions, turbid systems etc. Spring[13] has described problems with getting an absolutely pure solution with no traces of turbidity, (solution optiquement vide) and claims that solution purification with the help of electric current gives the best results.

§9. Let's consider now the theory of the reverse phenomenon of diaphragm currents. As above, we will restrict our considerations to the first approximation, which means that we will neglect the effect of the electric current generated by the movement of the liquid on this movement.

Let's start from the basic equation for small electric currents, which for our situation implies that the direct current and convection current together cannot lead to charge accumulation.

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[12] See: Quincke, *Wied Ann.* **59**, p. 417, 1896; Schweidler, *Sitzungaber. Wien. Ak.* **106**, p. 526, 1897; Heydweiller, *Wied. Ann.* **69**, p. 531, 1899; Graetz, *Drude Ann.* **1**, p. 530, 1900.

[13] *Bull. de Belg.* **200**. p. 174. 1899.

As the first component of the total potential

$$U = \varphi + \Phi + V$$

cannot contribute to current generation, the second term is assumed zero, the only condition is that expressed below in vector symbols:

$$\operatorname{div}\left[\frac{1}{\sigma}\Delta V + \varepsilon v\right] = 0$$

or in full form:

$$\frac{1}{\sigma}\Delta^2 V + \frac{\partial}{\partial x}(\varepsilon u) + \frac{\partial}{\partial y}(\varepsilon v) + \frac{\partial}{\partial z}(\varepsilon w) = 0. \tag{20}$$

Because of incompressibility:

$$\Delta^2 V = -\sigma\left(u\frac{\partial \varepsilon}{\partial x} + v\frac{\partial \varepsilon}{\partial y} + w\frac{\partial \varepsilon}{\partial z}\right). \tag{21}$$

As the current flowing along the normal to the surface $\frac{1}{\sigma}\frac{\partial V}{\partial n}$ must be zero, we get from the above the value of potential V

$$V = \frac{\sigma}{4\pi}\iiint \frac{u\frac{\partial \varepsilon}{\partial x} + v\frac{\partial \varepsilon}{\partial y} + w\frac{\partial \varepsilon}{\partial z}}{r}\,d\omega. \tag{22}$$

Knowing that the integrated quantity is different from zero only in the surface layer, we choose as a volume element $d\omega$ a layer of the thickness $d\zeta$, and area of dS, so $d\omega = d\zeta \cdot dS$, and – because ε is variable only in the direction of the normal, we can write

$$V = \frac{\sigma}{4\pi}\iiint \frac{v_\zeta}{r}\frac{\partial \varepsilon}{\partial \zeta}\,d\zeta\, dS.$$

For the points at a greater distance (great relative to δ) we can calculate the integral as:

$$V = \frac{\sigma}{4\pi}\iint \frac{dS}{r}\int v_\zeta \frac{\partial \varepsilon}{\partial \zeta}\,d\zeta. \tag{23}$$

The integral over $d\zeta$ can be developed by repeated partial integration, taking into account that the terms v_ζ, $\partial v_\zeta/\partial\zeta$ vanish on the surface, while $\partial\varphi/\partial\zeta$ and $\partial^2\varphi/\partial\zeta^2$ vanish at distances greater than δ,

$$4\pi\int_0^\delta v_\zeta \frac{\partial \varepsilon}{\partial \zeta} = -\int_0^\delta v_\zeta \frac{\partial^3 \varphi}{\partial \zeta^3}\,d\zeta = \int_0^\delta \frac{\partial^2 v_\zeta}{\partial \zeta^2}\frac{\partial \varphi}{\partial \zeta}\,d\zeta. \tag{24}$$

Now, we should take into account the mechanical equation, derived according to eq. (5) but with $\Phi = 0$,

$$\frac{\partial P}{\partial \zeta} = \mu \Delta^2 v_\zeta, \tag{25}$$

where P satisfies the condition $\Delta^2 P = 0$ and on the surface layer it is continuously transformed into hydraulic pressure p. Therefore, P can be treated as constant within δ, while on the other hand, neglecting lower order components, the term $\Delta^2 v_\zeta$ can be replaced by $\frac{\partial^2 v_\zeta}{\partial \zeta^2}$. Therefore, the value of the integral is

$$\int \frac{\partial^2 v_\zeta}{\partial \zeta^2} \frac{\partial \varphi}{\partial \zeta} d\zeta = \frac{1}{\mu} \frac{\partial P}{\partial \zeta} (\varphi_l - \varphi_a).$$

So

$$V = \frac{\sigma}{4\pi} \frac{(\varphi_l - \varphi_a)}{4\pi\mu} \int\int \frac{\partial P}{\partial \zeta} \frac{dS}{r}, \tag{26}$$

and taking into account that $\Delta^2 P = 0$, we have

$$V = \sigma \frac{(\varphi_l - \varphi_a)}{4\pi\mu} P + \text{const.} \tag{27}$$

In view of the above, the potential difference for points internal to the fluid is

$$V_2 - V_1 = \frac{(\varphi_l - \varphi_a)}{4\pi\mu} \sigma (p_2 - p_1). \tag{28}$$

§10. The latter formula proves to be identical to the corresponding Helmholtz equation, but can be applied not only to the Poiseuille tubes but to any vessels in which slow motion of the liquid takes place.

Indeed, the results of the Quincke experiments, in which the varied parameters were the current of water, diaphragm thickness and cross-section, proved the proportionality between the electromotive force and actual pressure difference, and independence of the above-mentioned factors.

The relation to specific electrical resistance (resistivity) is indicated by the Quincke's remark that as a result of addition of salts or acids to water, the electromotive force considerably decreased. Unfortunately, the coefficients of conductivity were not determined, so the values of $(V_2 - V_1)/(p_2 - p_1)$ (e.g. for sulfur in water = 10 Volt/atmosphere), cannot be used to calculate $(\varphi_l - \varphi_a)$.

It should be noted that eqs. (15), (16) and (28) cannot be applied to turbulent motion, e.g. in wide pipes, in which the effect of the liquid inertia $\left[\varrho u \frac{\partial u}{\partial x} \dots\right]$ cannot be neglected.

It seems that the effect of inertia could explain the particular phenomenon of asymmetry, noted by K. Zakrzewski[14] if the tubes considered are coated with silver on the inside wall. The fact that the potential difference between the silver-coated inside wall of the tube and the electrode placed in front of the tube opening depended on the direction of water current resembles the known asymmetry of water current in such cases, the formation of a jet at the outflow, which – similarly as the corresponding electric phenomenon – is explained by the inertia of the liquid. In fact, the experiments of this type are beyond the proposed theory because we do not know if the silver-coated glass surface can be treated as insulator.

§11. At the beginning we mentioned the Lamb theory as competing with the Helmholtz theory. The difference between them is that Lamb rejects the assumption of the continuous transition in the double electric layer and treats this layer as a capacitor with plates at a distance d, covered with electric charge density $\varrho = (\varphi_l - \varphi_a)/4\pi d$. Moreover, instead of continuous variation of velocity in this layer, he assumes sliding of the inner plate of the capacitor at the velocity $u = lX/\mu$ driven by a tangential force X, while μ/l is the sliding coefficient. On the basis of so simplified and generalized assumptions, Lamb derives the formulae identical to eq. (15), (16) and (28), but his formulae instead of the term $(\varphi_l - \varphi_a)$ have $(l/d)(\varphi_l - \varphi_a)$.

It seems to me that it is impossible to assume 'a priori' that one or the other hypothesis is more or less reliable, also experiments cannot provide decisive evidence as we do not know l/d and $(\varphi_l - \varphi_a)$, unless it would be possible to measure the potential difference by another method.

However, if the measurements of diaphragm currents etc. between different substances proved that the quantity described by Helmholtz as $(\varphi_l - \varphi_a)$ and by Lamb as $l(\varphi_l - \varphi_a)/d$ would make a series of potentials[15], it could be indirect proof of the validity of Helmholtz theory, as the coefficients l/d must have rather random character.

Thus, we have three convenient methods for determination of potential difference of poor conductors that could be used as diaphragms similar to those used by Quincke, as we will no longer be restricted to the Poiseuille tubes.

It would be interesting to check on the basis of some larger experimental evidence a hypothesis put forward by Coehn saying that the potential difference of

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[14] *Rozprawy Ak. Um.* **39**. p. 258, 1900.

[15] The reverse argumentation would not be justified because I do not think that the existence of such a series of potentials should be necessary.

double layers on insulators is directly proportional to the dielectric constants of adjacent bodies. It is a large (are) area for experimenters[16].

§12. Let us go back to the hypothesis mentioned at the beginning, that was proposed as an attempt to explain the astonishing stability of certain turbid solution in terms of the same electric phenomena. Small particles falling towards the bottom must generate currents, similar to the diaphragm currents, that affect their motion and counteract their falling movement. This explanation is supported by great sensitivity of these emulsions to an increase in conductivity of the solution caused by addition of minimum amount of an electrolyte that is sufficient to initiate precipitation. Quantitative calculation of this phenomenon is beyond the scope of our theory because we have neglected the impact of the secondary phenomenon on the original one, although we will at least try to give an idea on the order of magnitude of this impact.

The reasoning can be made along two ways.

α) The distribution of potential V in the vicinity of the ball moving in the liquid at a velocity c is proportional to pressure

$$p = \frac{3}{2}\frac{c\mu a x}{r^3}$$ [17]

according to the equation

$$V = \frac{(\varphi_l - \varphi_a)}{4\pi}\frac{3}{2}\frac{ca\sigma x}{r^3} = \frac{(\varphi_l - \varphi_a)}{4\pi}\frac{3}{2}\frac{ca\sigma\cos\theta}{r^3}. \tag{29}$$

The tangential component of electromotive force equal to

$$\frac{\partial V}{\partial(a\theta)} = \frac{(\varphi_l - \varphi_a)}{4\pi}\frac{3}{2}\frac{c\sigma\sin\theta}{a^2}$$

would produce in the liquid for which eq. (13) is satisfied, a movement described

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[16] The relation between the potential difference at double electric layer and the dielectric constant K follows directly from the theory, if the equation for charge density is written in the form

$$\varepsilon = -\frac{K}{4\pi}\frac{\partial^2\varphi}{\partial n^2}.$$

The neglect of dielectric constant K in the theory of endosmosis has prompted the Coehn hypothesis, which has been mentioned by the author in the later paper (Graetz, *Handbuch der Elecktr., u. d. Mag*).

[17] See e.g.: Lamb, *Hydrodynamics*, p. 530.

by the velocity

$$\left.\begin{aligned} u &= \frac{\partial}{\partial x} \\ v &= \frac{\partial}{\partial y} \\ w &= \frac{\partial}{\partial z} \end{aligned}\right\} \left(\frac{(\varphi_l - \varphi_a)}{4\pi}\right)^2 \frac{\sigma c x}{\mu a^2}\left(1 + \frac{a^3}{2r^3}\right), \tag{30}$$

At a greater distance from the ball this movement would correspond to a uniform current of the liquid characterized by the velocity

$$c' = \left(\frac{(\varphi_l - \varphi_a)}{4\pi}\right)^2 \frac{c\sigma}{a^2\mu}.$$

However, as the liquid is in a closed vessel, the liquid current will produce electroosmotic pressure of the magnitude

$$\frac{3}{2}c'\frac{\mu a x}{r^3},$$

counteracting the primary motion.

Thus, the resultant of the forces will satisfy the equilibrium condition

$$6\pi\mu a c\left[1 + \left(\frac{(\varphi_l - \varphi_a)}{4\pi}\right)^2 \frac{\sigma}{a^2\mu}\right] = g(\varrho - \varrho')\frac{4a^3\pi}{3}. \tag{31}$$

β) Let us now estimate the energy dissipated as a result of the electric current generated by V.

Calculating it from the general formula:

$$W = \iiint \frac{1}{\sigma}\left[\left(\frac{\partial V}{\partial x}\right)^2 + \left(\frac{\partial V}{\partial y}\right)^2 + \left(\frac{\partial V}{\partial z}\right)^2\right] d\omega,$$

we will get

$$W = \frac{6\sigma\pi c^2}{a}\left(\frac{(\varphi_l - \varphi_a)}{4\pi}\right)^2. \tag{32}$$

As this energy is generated at the expense of mechanical energy, we should add the force corresponding to the frictional drag $6\mu\pi a c$. Therefore, the ball movement will be described by the same equation (31) as above.

Therefore the expression

$$a = \frac{(\varphi_l - \varphi_a)}{4\pi}\sqrt{\frac{\sigma}{\mu}}$$

gives the maximum radius of particles for which the above force can be important. For instance substitution of the values characteristic of water:

$$\sigma = 10^9\ [\mathrm{Hg} = 1] = 1 \cdot 17 \cdot 10^{-7}\ [\mathrm{C.G.S.}],$$
$$(\varphi_l - \varphi_a) = 2\ \mathrm{Volt} = \frac{2}{300}\ [\mathrm{C.G.S.}],$$

we will get $a = 10^{-6}$ cm. Thus, this hypothesis cannot explain the stability of emulsions made of larger particles, e.g. of microscopic size. On the other hand, for so small particles the friction resistance is enough to restrict the particles velocities to extremely small values

$$c = \frac{2}{9}\frac{a^2}{\mu}g(\varrho - \varrho') = 10^{-8}\ \mathrm{cm/sec},$$

which means that such particles would fall by one centimeter in the whole year. Of course it is doubtful if for so small particles the thickness of the layer δ could still be treated as infinitesimally small, anyway, our considerations have shown that such an explanation is insufficient.

§13. Let us be aware of a so far unobserved detail.

Similarly as in (12 β) from the increase in energy dissipated as a result of the diaphragm current we could infer an equivalent increase in mechanical resistance, in the same manner from analysis of the mechanical energy dissipated during electric endosmosis we could also infer an increase in the electric current.

The mechanism of this phenomenon directly implies that it must be related to the convectional electric current in the surface layers.

The phenomenon of surface conductivity, which may have some significance in poor conductors, will be the subject of a separate paper.

§14. The importance of these phenomena is not restricted to the examples discussed in this paper, they are of greater significance for physics. I would like to draw your attention to a few facts that deserve to be experimentally studied in more detail.

First of all, as has been already noted by Helmholtz, in the simplest case electric charges appear as a result of friction. Probably explanation of other phenomena of this type e.g. in solid bodies, will be analogous and their experimental studies should be performed in a similar way.

Let's also note that this theory probably applies also to gases. As Quincke observed, small bubbles of air, hydrogen and other gases in water move towards the anode. Probably the reverse phenomenon is generation of electricity in liquid hitting against the wall (Lenard[18]) and in water through which air bubbles are passed (Kelvin[19]).

Since air can also act as a conductor, e.g. in Geissler tubes, then we should expect the electroosmotic phenomenon, that is generation of pressure difference between the anode and cathode.[20]

On the other hand, a phenomenon analogous to "electric transportation" can be the purification of air from dust, smoke etc., by electric discharge, in which polarity plays a pronounced role.

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[18] *Wied. Ann.* **46**, p. 584, 1892.

[19] *Proc. Roy. Soc. London* **57**, p. 335, 1895.

[20] Such a phenomenon has been observed by Ségny, *Comptes Rendus* **127**, p. 385, 1899.