SOME NOTES ON THE THEORY OF ELECTRO-OSMOSIS. PART I.

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1. Introduction. The phenomenon of electro-osmosis was, at first, discovered by Reuss, Russian scientist, on 1808. Since then, many authorities have been in research on this subject. The phenomenon takes place in the following familiar experiment: the bath is separated by a membrane (for examples, porcelain, texture and glass powder etc.) as shown in Fig. 1. The electrodes are inserted in each chamber and the electromotive-force is applied between them. Then, the liquid flows out through capillaries of membrane under the applied electric force, the level of one chamber being raised up over that of the other.

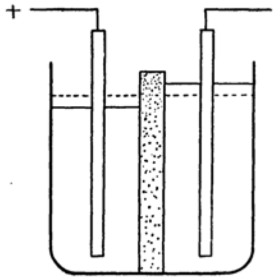

Fig. 1.

The mechanism for this phenomenon is considered to be due to the electric double layers existed on the surface of capillary wall. This theory was chiefly treated by Helmholtz, Lamb, Smoluchowski and others, and the very simplified following equation was dedused:

$$W=\frac{\zeta VDA}{4\pi\mu L}, \qquad (1)$$

where W is the quantity of liquid flowed out per unit time; A, the area of capillary; L, the length of capillary; ζ, the potential of double layers; V, the applied electric field; D, the dielectric constant of liquid; μ, the coefficient of viscosity of liquid.

But, we can also treat the theory of electro-osmosis in far more details under some assumptions. The purpose of this paper is to present one of these methodes carried out, as follows.

2. Electrical Condition in Capillary. Generally, at the surface of separation of two different materials, the ionic balance differs from that in the inner part of them. One kind of ion, positive or negative, accumulates there over the another kind of ion, according to the electrical properties of these materials.

The electrical condition in capillary is an interesting problem on the physical point of view. In our problem, the variation in configuration of electric charges takes place only in the capillary, because the solution in capillary are far more ionized than the materials of capillary wall.

For the convenience to the mathematical treatment, here we use the cylindrical coordinates (r, θ, z), z-axis being coincided with the axis of capillary as shown in Fig. 2. To neglect the effect of its terminals, the capillary is of infinite length for both directions of z.

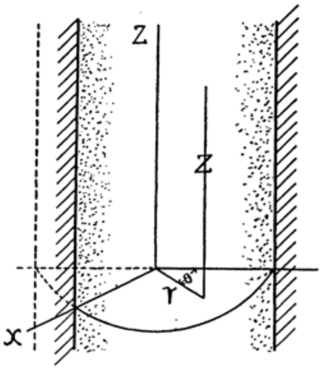

Fig. 2.

Let φ, be the potential;
ρ, the electric charge;
T, the absolute temperature;
C, the concentration;
D, the dielectric constant of liquid;
R, the radius of capillary;
k, Boltzmann's constant;
F, Faraday's constant.

The following two relations are established in this case:

(a) Equation of Poisson.

$$\Delta\varphi=-\frac{4\pi}{D}\rho \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

(b) Maxwell-Baltzmann's distribution law. For the sake of simplicity, we take up the special case of monovalent ion as follows. That is,

$$\rho=F(C_+-C_-) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (3)$$

$$=FC_0\left(e^{-\frac{\varphi F}{kT}}-e^{\frac{\varphi F}{kT}}\right)$$

$$=-FC_0\sinh\frac{\varphi F}{kT} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (4)$$

where C_0 is the concentration for $\varphi=0$.

For the small quantity of $\left(\frac{\varphi F}{kT}\right)$, we can neglect the higher power of $\left(\frac{\varphi F}{kT}\right)$ and obtain the simplified equation:

$$\rho=\frac{2C_0F^2}{kT}\varphi\,, \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (5)$$

From (2) and (5),

$$\Delta\varphi=\frac{\partial^2\varphi}{\partial r^2}+\frac{1}{\gamma}\frac{\partial\varphi}{\partial r}=\frac{8\pi F^2C_0}{DkT}\varphi=\varkappa^2\varphi\ , \quad\ldots\ldots\ldots\ldots \quad (6)$$

where

$$\varkappa=\sqrt{\frac{8\pi F^2C_0}{kDT}}\ , \text{ say } \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

Also from (5) and (7),

$$\rho=\frac{D}{4\pi}\varkappa^2\varphi\ \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

The solution of (6) is given by;

$$\varphi=C_1J_0(i\varkappa r)+C_2Y_0(i\varkappa r)\ , \quad\ldots\ldots\ldots\ldots \quad (9)$$

where C_1 and C_2 are the integration constants to be determined from the boundary conditions; J_0 and Y_0 are Bessel functions of zeroth order of first and second kind respectively.

For $r=0$, φ does not become infinite. That is, $C_2=0$.

At the surface of separation (capillary wall) $r=R$, we have

$$\begin{cases} \qquad\varphi=\varphi_0\ , & \ldots\ldots\ldots\ldots \quad (10)\\ \text{and}\quad \dfrac{\partial\varphi}{\partial r}=-\dfrac{4\pi}{D}\eta_0\ , & \ldots\ldots\ldots\ldots \quad (11)\end{cases}$$

where η_0 is the surface density of charge at the separation.

From (10),

$$C_1=\frac{\varphi_0}{J_0(i\kappa R)}\ \ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

or, from (11),

$$\left[\frac{\partial\varphi}{\partial r}\right]_{r=R}=-C_1i\varkappa J_1(i\varkappa R)=-\frac{4\pi}{D}\eta_0\ ,$$

$$C_1=\frac{4\pi N_0}{Di\varkappa J_1(i\varkappa R)}\ . \quad\ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

But, from equation (8), the total charge in capillary per unit length is given by

$$2\pi\int_0^R\rho.r\,dr=2\pi\frac{D}{4\pi}\varkappa^2C_1\int_0^R rJ_0(i\varkappa r)dr$$

$$=-\frac{2\pi R D i\varkappa J_1(i\varkappa R)C_1}{4\pi}$$

$$=-2\pi R\eta_0\;, \tag{14}$$

This is, the total charge in capillary is equal to the total surface charge at the surface of capillary wall in amount but with opposite sign. This is the condition which satisfies our problems.

The distribution of potential is:

$$\varphi=\varphi_0\frac{J_0(i\varkappa r)}{J_0(i\varkappa R)} \quad \text{[from (12),]} \tag{15}$$

$$=\frac{4\pi\eta_0 J_0(i\kappa r)}{D i\varkappa J_1(i\varkappa R)} \quad \text{[from (13),]} \tag{16}$$

and

$$\left.\begin{aligned}[\varphi]_{r=0}=\varphi^*&=\frac{\varphi_0}{J_0(i\varkappa R)}\\ &=\frac{4\pi\eta_0}{D i\varkappa J_1(i\varkappa R)}\end{aligned}\right\} \tag{17}$$

and

$$[\varphi]_{r=R}=\varphi_0=\frac{4\pi\eta_0 J_0(i\varkappa r)}{D i\varkappa J_1(i\varkappa R)} \tag{18}$$

The distribution of charge is:

$$\rho=\frac{D\varkappa^2\varphi_0 J_0(i\varkappa r)}{4\pi J_0(i\varkappa R)} \quad \text{[from (12),]} \tag{19}$$

$$=\frac{\varkappa\eta_0 J_0(i\varkappa r)}{i J_1(i\varkappa R)} \quad \text{[from (13),]} \tag{20}$$

and

$$\left.\begin{aligned}[\rho]_{r=0}=\rho^*&=\frac{D\varkappa^2\varphi_0}{4\pi J_0(i\varkappa R)}\\ &=\frac{\varkappa\eta_0}{i J_1(i\varkappa R)}\end{aligned}\right\} \tag{21}$$

and

$$[\rho]_{r=R}=\frac{D\varkappa^2\varphi_0}{4\pi}=\frac{\varkappa\eta_0 J_0(i\varkappa R)}{i J_1(i\varkappa R)} \tag{22}$$

The distribution of charges is shown in Fig. 3.

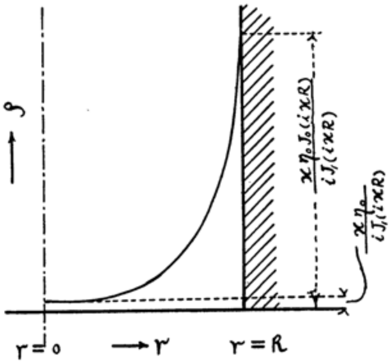

Fig. 3.

From the fact mentioned in (14), we can replace this configuration by the effective condenser. This is the so-called condenser-like-configuration of electrical double layers. Let a and b the radii of inner and outer concentric cylinders respectively, then the capacity per unit length is given by $\frac{D}{2\log\left(\frac{b}{a}\right)}$. Therefore, putting δ the distance between two concentric cylinders, we have

$$\frac{D}{2\log\left(\frac{b}{a}\right)}=\frac{D}{2\log\frac{R}{R-\delta}}=q\text{ , say} \quad\dots\dots\dots\dots \quad (24)$$

Therefore, we have $\delta=R\left(1-e^{-\frac{D}{2q}}\right)$, ... (25)

where $$q=\frac{2\pi\int\rho r dr}{\varphi_0-\varphi^*}=\frac{RD\varkappa\{-iJ_1(i\varkappa R)\}}{2\{J_0(i\varkappa R)-1\}} \quad\dots\dots\dots\dots \quad (26)$$

Actually, in some cases, one part of ions in capillary are adsorbed on the capillary wall by the specific adsorption, as shown in Fig. 4. Then the distributions of potential and charge are far more complicate than that discussed above.(1) But, here we will not enter into these subjects further.

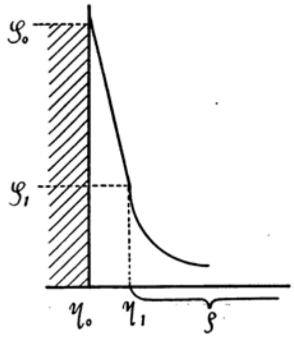

Fig. 4.

And, for the mixture of polivalent ions, the equations become complicate, but the just similar considerations are also to be carried out.

3. Electro-osmotic Flow in Capillary. Let us consider the steady motion of liquid through capillary under applied electric force.

Let us take the coordinates the same used in Section 2, and also

v, be the velocity of flow;
p, the pressure;

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(1) Cf. O. Stern, *Z. Elektrochem.*, **30** (1923), 508.

d, the density;
μ, the coefficient of viscosity;
ν, the kinematic coefficient of viscosity $(=\mu/d)$;
E, the applied electric field intensity.

For a considerable small capillary, it is questionable whether μ, ν and D are given by their normal values or not. Although this problem is important, it is not yet been made clear now.

The lines of flow in this case are all parallel to the z-axis:

$$v_x = v_y = 0 \ .$$

As the liquid is considered to be imcompressible, we have also

$$\frac{\partial v_z}{\partial z} = \frac{\partial v}{\partial z} = 0 \, ,$$

that is, v is the function of x and y, but not of z.

The electric charges are set in motion under the applied electric force toward the electrode of opposite sign. And the liquid element is, too, acted by the force due to the resultant volume charges which are contained in it. Here, we assume that the distribution of charges in this case is the same as that discussed in section 2 and that the body force acting on the liquid element is equal to that on the resultant volume charges in it. Then, the body force is given by:

$$K = EF(C_+ - C_-) = \rho E = \rho^* J_0(i\varkappa r)E = K_0 J_0(i\varkappa r) \ , \ \ldots\ldots \quad (27)$$

where

$$K_0 = E\rho^* = \frac{\varkappa E \eta_0}{iJ_1(i\varkappa R)} \ . \ \ldots\ldots\ldots\ldots\ldots\ldots \quad (28)$$

Resulting from these considerations, the following equation of hydrodynamics for viscous liquid is applicable:

$$K - \frac{1}{d}\ \mathrm{grad}\, p + \nu \Delta v = 0 \ , \ \ldots\ldots\ldots\ldots\ldots\ldots \quad (29)$$

or

$$K_0 J_0(i\varkappa r) - \frac{1}{d}\frac{\partial p}{\partial z} + \nu \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial v}{\partial r}\right) = 0 \ . \ \ldots \quad (30)$$

Differentiating (30) with z, we have

$$\frac{\partial^2 p}{\partial z^2} = 0 \ ,$$

therefore

$$\frac{\partial p}{\partial z} = a \ . \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (31)$$

where a is the integration constant.

Inserting (31) into (30) and integrating with r twice, then we have

$$v=\frac{a}{4\mu}r^2-\frac{K_0}{\varkappa^2\nu}J_0(i\varkappa r)+A\log r+B\ . \quad \ldots\ldots\ldots \quad (32)$$

where A and B are the integration constants. The boundary conditions are:

(i) v is not infinite at $r=0$; $A=0$. (33)

(ii) The liquid is not in motion on the surface of capillary wall;

$$[v]_{r=R}=0\ .$$

So

$$B=\frac{K_0 J_0(i\varkappa R)}{\varkappa^2\nu}-\frac{a}{4\mu}R^2\ . \quad \ldots\ldots\ldots\ldots \quad (34)$$

Therefore,

$$v=\frac{1}{4}\frac{a}{\mu}(r^2-R^2)+\frac{K_0}{\nu\varkappa^2}[J_0(i\varkappa R)-J_0(i\varkappa r)]\ . \quad \ldots\ldots \quad (35)$$

Now, let the length of capillary be L $(L\gg R)$ and the pressures at two ends be p_1 and p_2 respectively, then

$$\frac{\partial p}{\partial z}=a=-\frac{(p_1-p_2)}{L}\ . \quad \ldots\ldots\ldots\ldots\ldots \quad (36)$$

So

$$v=\frac{(p_1-p_2)}{4\mu L}(R^2-r^2)+\frac{K_0}{\nu\varkappa^2}[J_0(i\varkappa R)-J_0(i\varkappa r)]\ . \quad \ldots\ldots \quad (37)$$

If the pressure difference between two ends of capillary be very small compared with the body force acting on the liquid, then we can neglect the first term in (37):

$$v'=\frac{K_0}{\nu\varkappa^2}[J_0(i\varkappa R)-J_0(i\varkappa r)]\ , \quad \ldots\ldots \quad (38)$$

which is shown in Fig. 5.

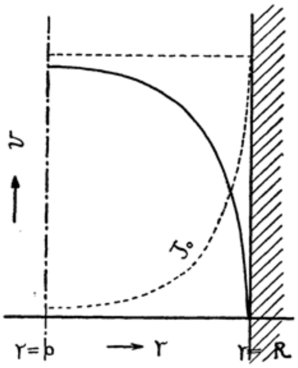

Fig. 5.

The quantity of liquid flowed out through capillary per unit time is

$$W=2\pi\int_0^R vr\,dr$$

$$=\frac{\pi(p_1-p_2)}{8\mu L}R^4+\frac{2\pi K_0}{\nu\varkappa^2}\left[\frac{R^2}{2}J_0(i\varkappa R)+\frac{iRJ_1(i\varkappa R)}{\varkappa}\right]. \quad \ldots \quad (39)$$

Also, if we neglect the first term, we obtain

$$W' = \frac{\pi R^2 K_0}{\nu \varkappa^2} \left[J_0(i\varkappa R) + \frac{2iJ_1(i\varkappa R)}{\varkappa R} \right] . \quad \dots\dots\dots \quad (40)$$

If we can balance the hydrostatic force and the electric force,

$$W = 0 \ ,$$

or

$$\frac{p_1 - p_2}{L} = \frac{P}{L} = -\frac{8\mu K_0}{\nu \varkappa^2 R^2} \left[J_0(i\varkappa R) + \frac{2iJ_1(i\varkappa R)}{\varkappa R} \right] . \quad \dots\dots \quad (41)$$

The electric charges are transfered by the flow of liquid. This amount per unit time is given by the equation:

$$\begin{aligned} Q &= 2\pi \int_0^R \rho v r \, dr \\ &= 2\pi \int_0^R r \rho^* J_0(i\varkappa r) \left[\frac{a}{4\mu} (r^2 - R^2) + \frac{K_0}{\nu \varkappa^2} \Big(J_0(i\varkappa R) - J_0(i\varkappa r) \Big) \right] dr \\ &= \frac{\pi \rho^* a R^2}{\mu \varkappa^2} J_2(i\varkappa R) + \frac{\pi \rho^* K_0 R^2}{\nu \varkappa^4} \left\{ \Big[J_0 i\varkappa R \,) \Big]^2 - 2 \left(\frac{\varkappa}{R} \right) \Big[J_0(i\varkappa R) J_1(i\varkappa R) \Big] \right. \\ &\qquad \left. + \Big[J_1(i\varkappa R) \Big]^2 \right\} . \quad \dots\dots\dots\dots\dots\dots \quad (42) \end{aligned}$$

When $a=0$, the first term in (42) vanishes as in the equation (38) and (40).

4. Electric Current through Capillary. In the present section, we consider the electric current through capillary. From Section 2, we can obtain the values of the charges:

$$\rho_+ = FC_0 e^{-\frac{\varphi F}{kT}} \ . \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (43)$$

$$\doteqdot FC_0 \left\{ 1 - \frac{\varphi F}{kT} \right\} = FC_0 \left\{ 1 - \frac{\rho^*}{2FC_0} J_0(i\varkappa r) \right\} . \quad \dots\dots \quad (44)$$

$$\rho_- = FC_0 e^{-\frac{\varphi F}{kT}} \ . \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (45)$$

$$\doteqdot FC_0 \left\{ 1 + \frac{\varphi F}{kT} \right\} = FC_0 \left\{ 1 + \frac{\rho^*}{2FC_0} J_0(i\varkappa r) \right\} . \quad \dots\dots \quad (46)$$

The electric current (I) required is given by the equation:

$$i = E(\rho_+ m_+ + \rho_- m_-) \ , \quad \dots\dots\dots\dots\dots\dots \quad (47)$$

and

$$I=2\pi\int_0^R ir\,dr \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (48)$$

where m_+ and m_- are the mobilities of ions. The electro-osmotic flow takes place in capillary as has treated in Section 3. For example, let the electro-osmotic flow be directed from the positive electrode to the negative, then, the negative charges are prevented their motion by the flow, and contrary to it, the positive charges are promoted their motion. Therefore, the mobility is smaller for negative ions and greater for positive ones than the normal values, and moreover differs from place to place as velosity does. But, as far as this flow is very small, this deviation is also small. In general, the mobility will be smaller in such a small capillary than in a normal free state.

But assuming here m_+ and m_- to be their normal values, then we have from (44), (46), (47) and (48),

$$i=EFC_0\left[\left\{1-\left(\frac{\rho^*}{2FC_0}\right)J_0(i\varkappa r)\right\}m_+ +\left\{1+\left(\frac{\rho^*}{2FC_0}\right)J_0(i\varkappa r)\right\}m_-\right]. \quad (49)$$

and

$$I=2\pi EFC_0\int_0^R\left[(m_+ +m_-)r-(m_+ -m_-)\left(\frac{\rho^*}{2FC_0}\right)rJ_0(i\varkappa r)\right]dr$$

$$=EFC_0\pi R^2(m_+ +m_-)\left\{1+\left(\frac{m_+ -m_-}{m_+ +m_-}\right)\left(\frac{\rho^*}{2FC_0}\right)\left(\frac{iJ_1(i\varkappa R)}{\varkappa R}\right)\right\}. \quad (50)$$

The first term, $EFC_0\pi R^2\ (m_+ + m_-)$, is the current established in the large vessel. Therefore, the current differs in the capillary by the amount equal to the second term.

Summary

(1) Under some assumptions, the distributions of potential and electric charge in capillary are given by the equations (15)—(22) . . . . (Section 2.)

(2) The quantity of liquid flowed out electro-osmotically W' is given by the equation (40), and $W'/\pi R^2$ is expressed by the function of radius R. The relation between permeability of membrane and electro-osmotic transfer has already been pointed out⑴ to be different from that given by the Helmholtz's equation in which $W'/\pi R^2$ is constant for any R, although it is only considered to be caused from the "free-osmosis"—that is, equivalent to the first term in right hand member of equation (39). . . . . (Section 3.)

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(1) A. Strickler and J. H. Mathews, *J. Am. Chem. Soc.*, **44** (1922), 1647.

(3) The current in capillary differs from that in the large vessel, because of its non-uniform distribution of electric charge. This is given by the equation (50). And, the relation between so-called surface conduction and ζ-potential seems to be slight, as D.R. Briggs(1) has stated. (Section 4.)

The writer wishes to express his hearty thanks to Prof. Setoh for his kind advice.

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(1) D. R. Briggs, "Colloid Symposium Monograph", **4** (1928), 41.