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ON ELECTRO-OSMOSIS AND STREAMING-POTENTIALS
IN DIAPHRAGMS.

II. General quantitative relationship between electro-kinetic effects

BY

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A general proof is given for the equality of the streaming-potential E/P and the electro-osmotic transport of liquid V/I , independent of the structure of the diaphragm. The presence of surface conductance and even inhomogeneity of the material from which the diaphragm is constructed, does not impair this relation. Three other relations involving also the streaming current and the electro-osmotic counter pressure, can easily be derived on the same base.

The proof is given by two independent methods, one method using a model of a diaphragm, which consists of a network of simple capillaries, the other treatment being based upon the thermodynamics of irreversible processes.

§ 1. Introduction.

In a previous paper ¹⁾ proof has been given that the relation of *Saxen* ²⁾ between streaming-potential and electro-osmosis

$$(E/P)_{I=0} = (V/I)_{P=0} \dots \dots \dots (1)$$

is valid for a "diaphragm" consisting of a number of cylindrical capillaries connected either in series or parallel to each other, irrespective of the dimensions of the individual capillaries and of the presence of surface conductance. In this paper the proof will be extended to the case of a completely irregular network of capillaries which need not have a circular cross-section and need not be composed of the same material. In the third section of this paper the proof will be given by the methods of non-equilibrium thermodynamics ³⁾, making use of *Onsager's* reciprocal relations ⁴⁾. Both these treatments allow a simple derivation of three other relations between electrokinetic effects, viz.

¹⁾ J. Th. G. Overbeek and P. W. O. Wijga, *Rec. trav. chim.* 65, 556 (1946).

²⁾ U. Saxen, *Wied. Ann.* 47, 46 (1892).

³⁾ I. Prigogine, *Etude thermodynamique des phénomènes irréversibles*, Liège 1947.

⁴⁾ L. Onsager, *Phys. Rev.* 37, 405 (1931); 38, 2265 (1931); H. B. G. Casimir, *Rev. Mod. Phys.* 17, 343 (1945).

$$(I/P)_{E=0} = (V/E)_{P=0} \quad (2)$$

$$(E/V)_{I=0} = (P/I)_{V=0} \quad (3)$$

$$(I/V)_{E=0} = (P/E)_{V=0} \quad (4)$$

In the left hand members of these relations E is the streaming potential (at zero current), I the streaming current (at zero potential difference) for a pressure difference P or a transport of liquid V through the diaphragm; in the right hand members V is the volume of liquid transported (at zero pressure difference), P the electro-osmotic counter pressure developed (at zero liquid transport) by a potential difference E or a current I through the diaphragm.

§ 2. The diaphragm treated as a network of capillaries.

a. *Electro-osmosis in a single capillary.*

Imagine a capillary of length l and constant cross-section of arbitrary form, filled with a liquid and connected at both ends to reservoirs containing the same liquid. In the liquid, at the interface with the capillary wall, an electrical double layer will generally be present characterised by a charge density ρ and a potential ψ , the potential in the bulk of the liquid being taken as zero.

When now a potential difference E is applied to the ends of the capillary and the pressure is kept constant in the whole system, an electro-osmotic transport of liquid equal to v cm³/sec will arise. This transport is caused by the force, exerted by the potential difference E on the charge ρ and which drags the liquid in which the charge is embedded with it. The stationary state is characterized by equality of electrical and viscous forces or by the relation ⁵⁾

$$\eta \left(\frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2} \right) = -\rho \frac{E}{l} \quad (5)$$

in which η is the viscosity and v_z the velocity of the liquid. The coordinate system is chosen with the z -axis in the direction of the capillary; E is the potential difference between $z = 0$ and $z = l$.

Application of *Poisson's* relation between charge density and potential results in the equation (ϵ is the dielectric constant of the liquid)

$$\eta \left(\frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2} \right) = + \frac{\epsilon E}{4\pi l} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \right) \quad (6)$$

⁵⁾ It is assumed that the distribution of charges in the double layer is independent of the current flowing. See *M. von Smoluchowski*, Bull. intern. acad. polon. sci., Classe sci. math. nat., 1903 p. 184.

which is satisfied by

$$v_z = -\frac{\epsilon E}{4\pi\eta l} (\zeta - \psi) \dots \dots \dots (7)$$

where ζ is the potential in the double layer at the surface of shear, where $v_z = 0$.

The total transport of liquid v is given by

$$v = \iint_{\text{cross section}} v_z \, dx \, dy = -\frac{\epsilon \zeta E}{4\pi\eta l} \iint \left(1 - \frac{\psi}{\zeta}\right) \, dx \, dy \dots \dots \dots (8)$$

or

$$v = CZE \dots \dots \dots (9)$$

where $Z = -\epsilon\zeta/4\pi\eta$ and C is a constant depending on the dimensions of the capillary and — usually only slightly — on the structure of the double layer.

b. *Streaming current in a single capillary.*

The same capillary used in the preceding section is now subjected to a pressure difference P between the ends. The mobile part of the double layer is carried away with the liquid flowing through the capillary. This constitutes the streaming current i , which is equal to

$$i = \iint v_z \rho \, dx \, dy = -\frac{\epsilon}{4\pi} \iint v_z \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2}\right) \, dx \, dy \dots \dots (10)$$

By two integrations by parts this expression is transformed into

$$i = \frac{\epsilon}{4\pi} \iint (\zeta - \psi) \left(\frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2}\right) \, dx \, dy \dots \dots \dots (11)$$

The flow of the liquid through the capillary satisfies the equation

$$\eta \left(\frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2}\right) = -\frac{P}{l} \dots \dots \dots (12)$$

By substituting (12) into (11) the streaming current is found to be

$$i = -\frac{\epsilon \zeta}{4\pi \eta} \frac{P}{l} \iint \left(1 - \frac{\psi}{\zeta}\right) \, dx \, dy = CZP \dots \dots (13)$$

and consequently to be governed by exactly the same constant CZ as the electro-osmotic flow (9).

c. *Stationary state in a network of capillaries.*

We will now treat the distribution of electric current and liquid flow in a network of capillaries, which may be considered as a good model for a diaphragm. The network consists of junction points,

numbered consecutively from 1 . . . n, connected by capillaries. The capillary connecting the points i and j is given the index ij. At the points 1 and n an electric current I and a liquid flow V enters, resp. leaves the network. See fig. 1.

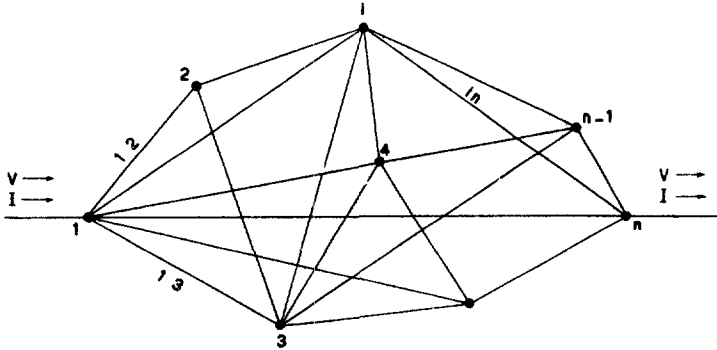


Fig. 1

Fig. 1. Schematic picture of the network.

The pressure and the potential at the junction point i are called P_i and E_i . The capillary ij then carries an electric current

$$i_{ij} = L_{ij} (E_i - E_j) + Z_{ij} C_{ij} (P_i - P_j) \dots \dots \dots (14)$$

and a flow of liquid

$$v_{ij} = F_{ij} (P_i - P_j) + Z_{ij} C_{ij} (E_i - E_j) \dots \dots \dots (15)$$

where L_{ij} is the electric conductivity and F_{ij} the hydrodynamic conductivity of the capillary.

The condition that no accumulation of electricity or of liquid may occur at any of the junction points, is expressed by the following $2n - 2$ independent linear equations

$$\left. \begin{aligned} \text{For } i = 1 \quad & \sum_2^n (E_j - E_i) L_{ij} + \sum_2^n (P_j - P_i) Z_{ij} C_{ij} = - I \\ \text{For } i = 2 \text{ to } & \sum_1^n \neq i (E_j - E_i) L_{ij} + \sum_1^n \neq i (P_j - P_i) Z_{ij} C_{ij} = 0 \\ \text{For } i = 1 \quad & \sum_2^n (E_j - E_i) Z_{ij} C_{ij} + \sum_2^n (P_j - P_i) F_{ij} = - V \\ \text{For } i = 2 \text{ to } & \sum_1^n \neq i (E_j - E_i) Z_{ij} C_{ij} + \sum_1^n \neq i (P_j - P_i) F_{ij} = 0 \end{aligned} \right\} (16)$$

Without loss of generality E_n and P_n are chosen equal to zero. The $2n - 2$ unknown potentials and pressures may then be solved from the equations (16). To make the solution more surveyable, eqs. (16) are written in the form

$$\left. \begin{aligned}
 E_1 (-\Sigma L_{1j}) + E_2 L_{12} + \dots + E_{n-1} L_{1, n-1} + P_1 (-\Sigma Z_{1j} C_{1j}) + \\
 + P_2 Z_{12} C_{12} + \dots + P_{n-1} Z_{1, n-1} C_{1, n-1} = -I \\
 E_1 L_{12} + E_2 (-\Sigma L_{2j}) + \dots + E_{n-1} L_{2, n-1} + P_1 Z_{12} C_{12} + \\
 + P_2 (-\Sigma Z_{2j} C_{2j}) + \dots + P_{n-1} Z_{2, n-1} C_{2, n-1} = 0 \\
 \vdots \\
 E_1 (-\Sigma Z_{1j} C_{1j}) + E_2 Z_{12} C_{12} + \dots + E_{n-1} Z_{1, n-1} C_{1, n-1} + P_1 (-\Sigma F_{1j}) + \\
 + P_2 F_{12} \dots + P_{n-1} F_{1, n-1} = -V \\
 E_1 Z_{12} C_{12} + E_2 (-\Sigma Z_{2j} C_{2j}) + \dots + E_{n-1} Z_{2, n-1} C_{2, n-1} + P_1 F_{12} + \\
 + P_2 (-\Sigma F_{2j}) \dots + P_{n-1} F_{2, n-1} = 0 \\
 \vdots
 \end{aligned} \right\} (17)$$

The solutions for E_1 and P_1 , which completely describe the electrokinetic behaviour of the diaphragm, are given by

$$\left. \begin{aligned}
 E_1 = \frac{-I \Delta(11)}{\Delta} - \frac{V \Delta(11')}{\Delta} \\
 P_1 = \frac{-\Delta(1'1)}{\Delta} - \frac{V \Delta(1'1')}{\Delta}
 \end{aligned} \right\} \dots \dots \dots (18)$$

where Δ is the determinant of the coefficients of eqs. (17) and $\Delta(ij)$ the subdeterminant corresponding to the element ij .

$$\Delta = \begin{vmatrix}
 & 1 & & 2 & & \dots & & n-1 & & 1' & & 2' & & \dots & & n-1' \\
 1 & -\Sigma L_{1j} & & L_{12} & & \dots & & L_{1, n-1} & & -\Sigma Z_{1j} C_{1j} & & Z_{12} C_{12} & & \dots & & Z_{1, n-1} C_{1, n-1} \\
 2 & L_{12} & & -\Sigma L_{2j} & & \dots & & L_{2, n-1} & & Z_{12} C_{12} & & -\Sigma Z_{2j} C_{2j} & & \dots & & Z_{2, n-1} C_{2, n-1} \\
 \vdots & & & & & & & & & & & & & & & \\
 1' & -\Sigma Z_{1j} C_{1j} & & Z_{12} C_{12} & & \dots & & Z_{1, n-1} C_{1, n-1} & & -\Sigma F_{1j} & & F_{12} & & \dots & & F_{1, n-1} \\
 2' & Z_{12} C_{12} & & -\Sigma Z_{2j} C_{2j} & & \dots & & Z_{2, n-1} C_{2, n-1} & & F_{12} & & -\Sigma F_{2j} & & \dots & & F_{2, n-1}
 \end{vmatrix}$$

As Δ is a symmetrical determinant, the subdeterminants 11' and 1'1 are identical and consequently the solution (18) may be written

$$\begin{aligned}
 E &= AI - BV \\
 P &= BI - DV \dots \dots \dots (19)
 \end{aligned}$$

in which A, B and D are coefficients determined by the structure of the diaphragm and the properties of the interfaces.

d. Relations between different electrokinetic effects.

Even when the coefficients A, B and D in eq (19) are not known

a. Production of entropy in electro-kinesis.

We consider two vessels containing a liquid of volume V^I and V^{II} , electrostatic potentials E^I and $E^{II} = E^I - E$ and hydrostatic pressure P^I and $P^{II} = P^I - P$. The vessels are connected by means of a diaphragm. The whole system is kept at a constant temperature T . The liquid in both vessels contains n components, $n - 1$ carrying charges z_1, z_2, \dots, z_{n-1} per unit of mass, whilst the remaining one is uncharged. The concentration of every component is the same in both vessels.

Our first aim will be to calculate the production of entropy due to irreversible processes in our system. This will allow us to determine the conjugated "currents" and "forces", in the sense of *Onsager's* theory. We may then establish linear relations between those "currents" and "forces", for which *Onsager's* reciprocal relations are valid.

Let us write *Gibbs' equation* for the first vessel in the form ⁷⁾

$$T dS^I = dU^I + P^I dV^I - \sum_1^{n-1} (\mu_i^I + z_i E^I) dM_i^I - \mu_n dM_n^I \quad (26)$$

where μ_i is the chemical potential and M_i the mass of component i . An analogous relation holds for vessel II.

We have

$$dM_i^I + dM_i^{II} = 0 \quad i = 1, \dots, n) \quad (27)$$

Thus the change of entropy of the total system is given by

$$dS = dS^I + dS^{II} = \frac{1}{T} \left\{ dU^I + dU^{II} + P^I dV^I + P^{II} dV^{II} - \sum_1^{n-1} dM_i^I (\Delta \mu_i + z_i E) - dM_n^I \Delta \mu \right\} \quad (28)$$

where $\Delta \mu_i = \mu_i^I - \mu_i^{II}$

Applying the first law of thermodynamics to the whole system we find

$$dQ = dU^I + dU^{II} + P^I dV^I + P^{II} dV^{II} \quad (29)$$

Inserting (29) in (28) we get for the change of entropy

$$dS = \frac{1}{T} \left\{ dQ - \sum_1^{n-1} dM_i^I (\Delta \mu_i + z_i E) - dM_n^I \Delta \mu \right\} \quad (30)$$

⁷⁾ The influence of the reactions at the electrodes has for simplicity been omitted from eq. (26). Inclusion of these reactions would only complicate the treatment without changing the fundamental result, which is contained in the entropy production in the diaphragm as given by eq. (31).

which may be separated into $d_1S = dQ/T$, the entropy supply from the surroundings and

$$d_2S = -\frac{1}{T} \left\{ \sum_1^{n-1} dM_i^I (\Delta\psi + z_i E) + dM_n^I \Delta\mu_n \right\} \dots \dots (31)$$

the entropy production in the irreversible process.

As

$$\Delta\mu_i = v_i P \dots \dots \dots (32)$$

where v_i is the partial specific volume of component i , we find by substituting (32) into (31)

$$d_2S = -\frac{1}{T} \left\{ \sum_1^{n-1} z_i E dM_i^I + \sum_1^n v_i P dM_i^I \right\} \dots (33)$$

As the total electric current I and the total flow of liquid V from vessel I to vessel II are given by

$$I = -\sum_1^{n-1} z_i \frac{dM_i^I}{dt} \text{ and } V = -\sum_1^n v_i \frac{dM_i^I}{dt} \dots \dots (34)$$

the entropy production per unit of time can be written ⁸⁾

$$T \frac{d_2S}{dt} = IE + VP \dots \dots \dots (35)$$

that is in the form of a sum of products of "currents" and "forces", as is necessary for the application of *Onsager's* relations.

b. *The phenomenological relations.*

In the region of small pressure and potential difference (in practice one never works beyond this region) the "currents" are linearly dependent upon the "forces" as is expressed in the following equations.

$$\begin{aligned} I &= L_{11}E + L_{12}P \\ V &= L_{21}E + L_{22}P \end{aligned} \dots \dots \dots (36)$$

It then follows immediately from *Onsager's* theorem of reciprocity that

$$L_{12} = L_{21} \dots \dots \dots (37)$$

⁸⁾ The hydrodynamic current is here the true current through the diaphragm and does not include possible volume changes at the electrodes. Likewise the potential difference E is the potential difference between the liquid in vessel I and vessel II with exclusion of possibly unequal potential drops at the electrodes. This choice of variables is in harmony with the kinetic treatment of § 2.

Relation (36) with the condition (37) can be easily transformed into the reciprocal relations

$$\begin{aligned} E &= R_{11}I + R_{12}V \\ P &= R_{21}I + R_{22}V \end{aligned} \quad \dots \quad (38)$$

$$R_{12} = R_{21} \quad \dots \quad (39)$$

which are equivalent to the kinetically derived eq. (19).

The four relations (22)—(25) can consequently be found again by this thermodynamic treatment.

§ 4. Conclusion.

By independent thermodynamic and kinetic treatments it has been shown that from the eight different possibilities of expressing electrokinetic experiments on a diaphragm, only three are independent, as the equations governing the phenomena contain only three independent constants. Two of these constants are simply related to the electric and hydrodynamic resistance of the diaphragm and only the third one is closely connected with double layer properties.

Therefore it is useless to carry out more than one kind of electrokinetic experiment. The interpretation of this experiment in terms of ζ -potential demands further considerations on at least one of the constants in eq. (19) and cannot be reached by thermodynamic means, but only by further analysis of a model. This will be done in a subsequent paper.

Finally it may be interesting to point out where the bridge between the two apparently very different treatments of § 2 and § 3 is to be found. The kinetic considerations of § 2a and § 2b lead to the conclusion that streaming current and electro-osmotic flow in a single capillary are governed by the same constant CZ, or that for a single capillary

$$(I/P)_{E=0} = (V/E)_{P=0}$$

Combination of this relation with eq. (36) leads immediately to the conclusion that for a single capillary $L_{12} = L_{21}$. So, what in one case is reached by the application of *Onsager's* relations to the whole system, is reached in the other case by a kinetic analysis on the constituent parts of the system.

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