RECUEIL DES TRAVAUX CHIMIQUES DES PAYS-BAS
publ. par la Soc. chim. néerl. ['s-Gravenhage (Hollande), Lange Voorhout 5]
T. 72, 2 (février 1953).
Soc. anon. d'éditions scientifiques D. B. CENTEN, Amsterdam.

541.18 : 532.71 : 537.362

ON ELECTRO-OSMOSIS AND STREAMING-POTENTIALS IN DIAPHRAGMS.

III. Electrokinetic effects in networks of capillaries

BY

J. TH. G. OVERBEEK and W. T. VAN EST
(Van 't Hoff Laboratory and Mathematics Institute, University of Utrecht).

Elektrokinetic effects in diaphragms are treated with the aid of a model consisting of a network of capillaries. With negligible surface conductance or when all capillaries have equal cross-sections the streaming-potential E/P and the electro-osmotic flow V/I are both equal to $\varepsilon\zeta/4\pi\eta \cdot R \cdot C$ where R and C are the resistance and the capacity of conductance of the network. In the presence of surface conductance, and for unequal cross-sections of the capillaries, the proportionality constant between E/P or V/I and RC may be either smaller or greater than $\varepsilon\zeta/4\pi\eta$ depending on the detailed structure of the diaphragm. The first case is the usual one. For a value larger than $\varepsilon\zeta/4\pi\eta$ rather exceptional conditions have to be fulfilled.

1. Introduction.

In the first paper of this series *) attention was drawn to the fact, that the well-known equations for the streaming potential (E/P) and the electro-osmosis (V/I)

$$E/P = -V/I = \varepsilon\zeta/4\pi\eta\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

are valid only when the surface conductance is negligible. Correcting for any inhomogeneity in the conductivity by eq. (2) leads only to the right value of the ζ-potential in the case of a single capillary or a number of parallel capillaries but not in the case of capillaries in series or in the case of a more complicated diaphragm.

$$E/P = -V/I = \frac{\varepsilon\,\zeta}{4\,\pi\,\eta} RC \equiv ZRC \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In this equation R is the actual resistance of the diaphragm and C its capacity of conductance, as determined by filling the diaphragm with a strongly conducting liquid, so that surface conductance and electrokinetic phenomena may be neglected.

---

*) *J. Th. G. Overbeek* and *P. W. O. Wijga*, Rec. trav. chim. **65**, 556 (1946). To be cited as **I.**

By the application of thermodynamics of irreversible processes the equality of E/P and V/I was proved in a very general way *).

In the present paper we want to investigate the proportionality constant (Z') between E/P or V/I and RC in the case of a general network of capillaries

$$E/P = -V/I = Z'RC \quad \ldots \ldots \quad (3)$$

In paper I it was demonstrated for a number of capillaries in series that

$$|Z'| \leqq |\varepsilon\zeta/4\pi\eta| \quad \ldots \ldots \quad (4)$$

and it was suggested that this relation is also valid in more general cases, in accordance with the apparent "depression of the ζ-potential" that is nearly always found with diaphragms filled with highly diluted electrolyte solutions.

We shall now show, however, that although an apparent depression of the ζ-potential is much more likely than the reverse, there may be some cases where $|Z'|$ is greater than $|\varepsilon\zeta/4\pi\eta|$.

2. Stationary states in a network.

As a model of a diaphragm we choose a network N of capillaries. The network consists of a number of junction points or nodes, labeled 1, 2 . . . ., n interconnected by capillaries. The capillary joining the nodes i and j is labeled (ij). The capillaries are supposed to be filled with the same liquid which may enter and leave the network at specified nodes, for instance at the nodes 1 and n. The capillaries are supposed to be of the same material so that $\varepsilon\zeta/4\pi\eta$ has the same value in the whole network.

Let L_{ij} be the electric conductivity, F_{ij} the hydrodynamic conductivity and C_{ij} the capacity of conductance of the capillary (ij). Further let P_i and E_i represent hydrostatic pressure and electric potential at the node i, and i_i and v_i the electric current and the flow of liquid leaving the network at that node. Then the stationary states, characterized by the fact that no accumulation of liquid or electricity takes place at any of the nodes, are described by (see papers I and II)

$$\left.\begin{aligned} \sum_{j \neq i} L_{ij}(E_j - E_i) + \sum_{j \neq i} ZC_{ij}(P_j - P_i) &= i_i \\ \sum_{j \neq i} ZC_{ij}(E_j - E_i) + \sum_{j \neq i} F_{ij}(P_j - P_i) &= v_i \end{aligned}\right\} i = 1, 2 \;\ldots\; n \quad (5)$$

$$\sum_i i_i = \sum_i v_i = 0$$

*) *P. Mazur* and *J. Th. G. Overbeek*, Rec. trav. chim. **70**, 83 (1951); to be cited as **II**.

Defining $L_{ii} = -\sum_{j \neq i} L_{ij}$ $C_{ii} = -\sum_{j \neq i} C_{ij}$ and $F_{ii} = -\sum_{j \neq i} F_{ij}$

the equations (5) take the more symmetrical form (6).

$$\left.\begin{aligned} \sum_{1}^{n} {}_j L_{ij} E_j + \sum_{1}^{n} {}_j Z C_{ij} P_j &= i_i \\ \sum_{1}^{n} {}_j Z C_{ij} E_j + \sum_{2}^{n} {}_j F_{ij} P_j &= v_i \end{aligned}\right\} i = 1, 2 \; . \; . \; . \; n \quad (6)$$

$$\Sigma\, i_i = \Sigma\, v_i = 0$$

The rigorous treatment of the equations (6) by the methods of linear algebra has been given by *van Est* *).

In this paper we follow a more intuitive way, using, where necessary, *van Est*'s results.

In the equations (6) the *i*'s and *v*'s are expressed in terms of the *E*'s and *P*'s. By solving these equations with respect to the *E*'s and *P*'s, these quantities can be expressed in terms of the *i*'s and *v*'s, by means of coefficients that can be derived from the *L*'s, *C*'s and *F*'s.

Taking the special case that only in the nodes 1 and n solution or electricity can enter or leave the network and defining

$$\left.\begin{aligned} & i_1 = I, \quad i_n = -I \qquad i_j = 0 \; (j = 2, 3, \; . \; n-1) \\ & v_1 = V \quad v_n = -V \qquad v_j = 0 \; (j = 2, 3, \ldots n-1) \\ & E_1 - E_n = E \\ & P_1 - P_n = P \end{aligned}\right\} \; . \; . \; . \; . \; (7)$$

the measurable quantities *I, V, E* and *P* are connected by the equations

$$\left.\begin{aligned} E &= \frac{a}{\lambda} I + Z b V \\ P &= Z b I + d V \end{aligned}\right\} \; . \; . \; . \; . \; . \; . \; . \; . \; (8)$$

The symmetry as expressed in the coefficient *Zb* derives from the symmetry in the orginal equations (5). The coefficient of *I* in the first equation has been written as a/λ to express the fact that this coefficient is roughly proportional to the reciprocal of the specific conductivity of the solution. Similarly the second coefficient has been written as *Zb* because this coefficient is zero when the ζ potential is zero. The coefficients *a, b* and *d* can be expressed in terms of all the L_{ij}'s, C_{ij}'s and F_{ij}'s (see *van Est l.c.*). The equations (8) are equivalent to eq. (18) of *Mazur* and *Overbeek* (*l.c.*).

The value of the different electrokinetic effects can now be easily

*) *W. T. van Est* and *J. Th. G. Overbeek*, to be published in Proc. Koninkl. Akad. Wetenschap. Amsterdam.

expressed in terms of a/λ, Zb, and d. In order to compare these values to the Z' of eq. (3) it is still necessary to derive expressions for R and C. R is the actual resistance of the network under conditions where the electro-osmotic movement is free to develop, that is when $P = 0$.

$$R = \left(\frac{E}{I}\right)_{P=0} = \frac{a}{\lambda} - \frac{Z^2 b^2}{d}. \quad \quad (9)$$

The capacity of conductance C is determined by filling the network with a liquid of high specific conductivity λ_0 and determining C from

$$C = \frac{I}{\lambda_0 E} \quad \quad (10)$$

For the network filled with this liquid, equations similar to (5) will hold but they are greatly simplified by the fact that the electrokinetic terms may be neglected and that

$$L^{\circ}_{ij} = \lambda_0 C_{ij} \quad \quad (11)$$

The first of the equations (8) then takes the simple form

$$E = \frac{a_0}{\lambda_0} I \quad \quad (12)$$

where a_0 is a function of all the $L_{ij}{}^{\circ}$'s or rather of all the C_{ij}'s. By comparing (10) and (12) C is found equal to $1/a_0$.

$$C = \frac{1}{a_0} \quad \quad (13)$$

From eq. (8) it follows that the streaming potential and the electro-osmotic flow can be expressed in the following way:

$$(E/P)_{I=0} = -(V/I)_{P=0} = \frac{Zb}{d}. \quad \quad (14)$$

Substituting this, and the values for R and C from eq. (9) and (13) in eq. (3) one finds

$$\frac{Zb}{d} = \frac{Z'}{a_0}\left(\frac{a}{\lambda} - \frac{Z^2 b^2}{d}\right) \quad \text{or}$$

$$\frac{Z}{Z'} = \frac{ad - Z^2 b^2 \lambda}{a_0 b \lambda} \quad \quad (15)$$

Consequently $\quad Z' \overset{<}{\underset{>}{=}} Z$

when

$$\Omega = ad - Z^2 b^2 \lambda - a_0 b \lambda \overset{>}{\underset{<}{=}} 0 \quad \quad (16)$$

The general determination of the value of Ω requires, however, a detailed knowledge of the structure of the diaphragm, which is rarely available.

In the following cases more definite conclusions can be drawn.

3. **Negligible surface conductance.**

When surface conductance is negligible, the electric conductivity of a capillary is simply the product of the capacity of conductance and the specific conductivity λ of the solution.

$$L_{ij} = \lambda\, C_{ij} \quad \ldots\ldots\ldots\ldots \quad (17)$$

In that case the first of the equations (6) runs

$$\Sigma_j\, C_{ij}(\lambda\, E_j + ZP_j) = i_i \quad \ldots\ldots\ldots \quad (18)$$

For streaming potential all i_i's are zero and the only solution of (18) is

$$\lambda\, E_j + ZP_j = \text{const.}$$

from which it follows immediately that

$$E/P = -Z/\lambda \quad \ldots\ldots\ldots \quad (19)$$

in agreement with the classical results of *von Smoluchowski* *). As in this case RC is equal to $1/\lambda$, Z and Z' are equal.

4. **Surface conductance not negligible; all capillaries of the same constant cross-section.**

When surface conductance is not negligible but all capillaries have the same cross-section, the electric conductivity of the capillary (ij) is given by

$$L_{ij} = \left(\lambda + \frac{\sigma S}{O}\right) C_{ij} = \lambda' C_{ij} \quad \ldots\ldots \quad (20)$$

where S is the circumference, O the area of a perpendicular cross-section through the capillary and σ the specific surface conductivity.

As this equation is similar to eq. (17) with only λ changed into λ', the value of the streaming potential is now

$$E/P = -Z/\lambda'$$

and as for this homogeneous network

$$RC = 1/\lambda'$$

we have again

$$Z = Z' \quad \ldots\ldots\ldots\ldots \quad (21)$$

*) *M. von Smoluchowski*, Graetz's Handbuch der Elektrizität und des Magnetismus 2, 379, Leipzig 1914.

5. Surface conductance not negligible; network with capillaries of nearly equal cross-section.

Having thus shown that, when all capillaries have equal cross-sections, $Z = Z'$ or $\Omega = 0$, we can express Ω for the case where one or more of the capillaries have a slightly deviating cross-section as

$$\Omega = \triangle^1 \Omega + \triangle^2 \Omega + \triangle^3 \Omega + \quad \dots \dots \quad (22)$$

where $\triangle^1\Omega$ is a linear function of the slight deviations in the L_{ij}'s, C_{ij}'s, and F_{ij}'s, $\triangle^2\Omega$ is a quadratic function of these deviations etc.

Van Est (*l.c.*) could generally prove that

$$\triangle^1 \Omega = 0 \quad \dots \dots \dots \quad (23)$$

and

$$\triangle^2 \Omega \geq 0 \quad \dots \dots \dots \quad (24)$$

Consequently, as far as only these first and second order terms are concerned, the apparent value of $|\zeta|$ may be *lower* than the actual one, but never higher. The sign of higher order terms depends on the detailed structure of the network, and thus may be either positive or negative. We might say that Ω as a function of the L_{ij}'s, C_{ij}'s and F_{ij}'s is a kind of multidimensional saddle with a very narrow descending part and a broad ascending one. This would explain qualitatively the fact that experimentally an apparent depression of the ζ-potential is often found but the reverse has never been shown to exist.

6. Apparent rise in ζ-potential in the case of three capillaries.

It might be instructive to give an example where actually in a very narrow region of dimensions an apparent rise in the ζ-potential can be calculated.

Consider the case of three cylindrical capillaries α, β and γ, all of equal length l, with radii:

$$r_\alpha = xr \qquad r_\beta = yr \qquad r_\gamma = r$$

connected as shown in figure 1.

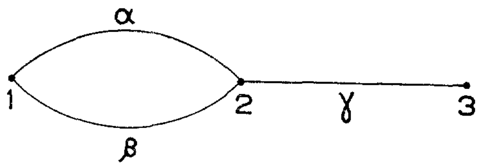

Fig. 1. "Network" of three capillaries.

According to paper I

$$L_{12} = L_\alpha + L_\beta = \frac{\pi \lambda r^2}{l}(x^2 + y^2) + \frac{2 \pi r \sigma (x + y)}{l}$$

$$C_{12} = C_\alpha + C_\beta = \frac{\pi r^2}{l}(x^2 + y^2)$$

$$F_{12} = F_\alpha + F_\beta = \frac{\pi r^4}{8 \eta l}(x^4 + y^4)$$

$$L_{23} = \frac{\pi \lambda r^2}{l} + \frac{2 \pi r \sigma}{l}, \quad C_{23} = \frac{\pi r^2}{l}, \quad F_{23} = \frac{\pi r^4}{8 \eta l}$$

According to eq. (15) p. 562 of paper I, which is correct up to quantities of the order Z^2,

$$\frac{Z'}{Z} = \frac{(C_{12}/L_{12}F_{12} + C_{23}/L_{23}F_{23})\,(1/C_{12} + 1/C_{23})}{(1/L_{12} + 1/L_{23})\,(1/F_{12} + 1/F_{23})} =$$

$$= \frac{\lambda r (x^2 + y^2)(x^2 + y^2 + 1)(x^4 + y^4 + 1) + 2 \sigma (x^2 + y^2 + 1)\{(x^4 + y^4)(x + y) + x^2 + y^2\}}{\lambda r (x^2 + y^2)(x^2 + y^2 + 1)(x^4 + y^4 + 1) + 2 \sigma (x + y + 1)(x^4 + y^4 + 1)(x^2 + y^2)}$$

Consequently

$$Z' \gtreqless Z \quad \text{if}$$

$$(x^2 + y^2 + 1)\{(x^4 + y^4)(x + y) + x^2 + y^2\} \gtreqless$$

$$(x + y + 1)(x^4 + y^4 + 1)(x^2 + y^2) \quad \text{or}$$

$$(x^4 + y^4 - x^2 - y^2)(x^2 + y^2 - x - y) \lesseqgtr 0 \;. \quad . \quad . \qquad (25)$$

As the left hand member consists of a product it can only be negative (in which case $Z' > Z$) when the two factors have different signs. Plotting the two equations

$$x^2 + y^2 - x - y = 0 \quad \text{and} \quad x^4 + y^4 - x^2 - y^2 = 0$$

in fig. 2 one sees that in the very narrow cross-hatched field Z' may be larger than Z, the maximum value of Z' being only slightly above Z, whereas for any other combination of x and y, $Z' < Z$, and may even approach zero as a limit.

Expanding the function (25) in the neighbourhood of the values $x = 1$ and $y = 1$ in a Taylor series we find:

$$(x^4 + y^4 - x^2 - y^2)(x^2 + y^2 - x - y) =$$

$$= 2(\triangle x + \triangle y)^2 + 7(\triangle x + \triangle y)(\triangle x^2 + \triangle y^2) +$$

fourth and higher order terms,

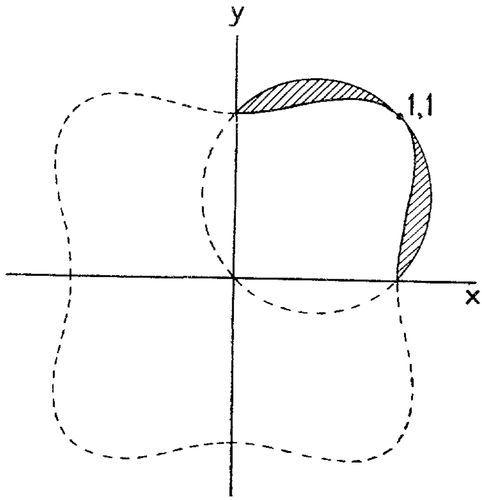

Fig. 2. A plot of the two curves $x^2 - y^2 - x - y = 0$ (circle) and $x^4 + y^4 - x^2 - y^2 = 0$ (fourth degree curve). Only between the two curves the combinations of x and y are found, which make $Z' > Z$.

where the first order term is absent, the second order term is essentially positive or zero and only the third order may be negative, leading to $Z' > Z$. This illustrates clearly the general principle indicated in § 5, that the apparent depression of the ζ-potential is a second order effect, but an apparent increase only of a higher order than the second.

7. Conclusions.

The conclusion of this analysis must be, that with negligible surface conductance or with a homogeneous network ζ can be accurately determined from electrokinetic experiments. For a more general network with surface conductance present, the value of ζ determined according to eq. (2) deviates from the real value of ζ. It is not possible to make a general statement on the sign of this deviation although an apparent depression of ζ is more likely than the reverse.

(Received June 26th 1952).