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ON ELECTRO-OSMOSIS AND STREAMING-POTENTIALS IN DIAPHRAGMS

BY

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It is mentioned that the streaming-potential E/P and the volume of liquid transported by electro-osmosis v/i are equal, independent of the structure of the diaphragm and independent of its surface conductance. The value of these ratios which, in the absence of surface-conductance equals $\varepsilon\zeta/4\,\pi\eta\lambda$ diminishes when surface-conductance is present. This decrease can be accurately taken into account when the diaphragm consists of a single capillary of constant diameter. In the case of real diaphragms, consisting of a network of capillaries of different shape and dimensions the correction factor for surface-conductance cannot be computed! It has been common practice to estimate the correction factor from the ratio of the observed to the calculated electric resistance of the diaphragm. This procedure is shown to be erroneous, leading to values of the ζ-potential that are essentially too low.

§ 1. *Introduction.*

Reliable evaluations of the ζ-potential are of fundamental importance to our insight in the structure of the electrochemical double layer and all connected problems, e.g. that of the stability of colloids. Although there exist a great variety of electrokinetic phenomena from which the ζ-potential can be evaluated, the interpretation of the experimental results proves to be interlaced with many pitfalls and difficulties. It will not be permissible to use electrokinetic phenomena as an exact basis for gaining insight in the structure of the double layer, before at least part of these difficulties have been cleared away. It is the purpose of this paper to show that the interpretation of observations of electro-osmosis and streaming-potentials in diaphragms contains a difficulty not realized up to now, which is caused by the presence of surface-conductance.

Smoluchowski 1) in his admirable analysis of electrokinetic phenomena showed that electro-osmosis and streaming-potentials in diaphragms can be interpreted by means of the equations (1a) and (1b) irrespective of the structure of the diaphragm, provided that the diameter of the smallest pores is large compared with the thickness of the double layer.

$$\frac{E}{P} = \frac{\varepsilon\zeta}{4\,\pi\eta\lambda} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1a)$$

$$\frac{v}{i} = \frac{\varepsilon\zeta}{4\,\pi\eta\lambda} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1b)$$

In these equations E is the streaming-potential at a pressure difference P, v is the volume of liquid transported by electro-osmosis at a current, i, ε is the dielectric constant, η the viscosity, λ the electric conductivity of the liquid and ζ the ζ-potential.

Different authors have shown that it is necessary to apply a correction to these equations, if the conduction through the diaphragm or the capillary is not exclusively determined by the bulk conductivity of the liquid, but is

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1) M. v. Smoluchowski, Bull. intern. acad. polon. sci., Classe sci. math. et nat. 1903, p. 184.

enhanced by surface conductance. In the case of a single capillary the corrected equations are given as 2)

$$\frac{E}{P} = \frac{v}{i} = \frac{\varepsilon\zeta}{4\,\pi\,\eta\left(\lambda + \frac{2\,\lambda_s}{r}\right)} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2a)$$

or

$$\frac{E}{P} = \frac{v}{i} = \frac{\varepsilon\zeta}{4\,\pi\eta\lambda}\,\frac{R_{exp}}{R_{calc}} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2b)$$

where λ_s is the specific surface conductivity, R_{exp} the observed electric resistance of the capillary and R_{calc} the resistance that would have been found in the absence of surface conductance.

Equation (2b) though strictly valid only for a single capillary has been applied to diaphragms as well 3). By observations of the streaming-potential and the electro-osmosis, one of us (Wijga, l.c.) has experimentally verified the equality of E/P and v/i both for single glass capillaries as well as for diaphragms of glass powder. The values of ζ, however, calculated according to (2b) from the experiments with diaphragms were distinctly too low, and the deviations were largest in dilute solutions, where, as is known, the surface conductance has its greatest influence.

In the following sections a model of a diaphragm will be given, allowing to perform a theoretical analysis of electrokinetic phenomena in diaphragms. The general equality of E/P and v/i can be proved. On the other hand a simple explanation is furnished of the apparent depression of the ζ-potential, mentioned above.

§ 2. A diaphragm may be represented as a network of capillaries interconnected in a multitude of ways. Each single capillary can be characterized by its electric resistance R_i, its hydrodynamic resistance W_i (= difference of pressure/volume passing per second) and its capacity of conductance C_i, C_i being defined as the reciprocal of the product of resistance and specific conductivity in the absence of surface conductance. In practice C_i may be determined by measuring the resistance of the capillary when filled with mercury or with a concentrated solution of an electrolyte.

For a capillary of radius r_i and length l_i

$$W_i = \frac{8\,\eta\,l_i}{\pi\,r_i^4},\quad R_i = \frac{l_i}{\pi r_i^2\left(\lambda + \frac{2\,\lambda_s}{r_i}\right)} \text{ and } C_i = \frac{\pi r_i^2}{l_i}$$

With the aid of these definitions equation (2b) may be converted into

$$\frac{E}{P} = \frac{v}{i} = \frac{\varepsilon\zeta RC}{4\,\pi\eta} = ZRC \quad . \ . \ . \ . \ . \ . \ . \quad (3)$$

where Z is written fore $\varepsilon\zeta/4\,\pi\eta$.

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2) See e.g. A. J. Rutgers, Trans. Faraday Soc. **36**, 69 (1940). P. W. O. Wijga, Thesis Utrecht, 1946.

3) D. R. Briggs, J. Phys. Chem. **32**, 641 (1928). H. B. Bull and R. A. Gortner, ibid. **35**, 307 (1931).

In the customary direct application of (3) to a diaphragm, R is its electrical resistance and C its capacity of conductance. These values of R and C may be determined in the same way as for a single capillary. They will be distinguished by a subscript as R_{cond} and C_{cond}.

It is, however, possible to replace a network of capillaries by a simpler one or even by a single capillary, having the same ζ-potential as the original capillaries, suitable dimensions and a suitable value of the surface-conductivity (that is suitable values of R, W and C). Such a substitution can always be carried out without any further change in the electric and hydrodynamic conditions outside the diaphragm. So this single capillary would show the same values of E/P or v/i as the original network. The values of R, W and C of this ultimate capillary, to which equation (3) may be confidently applied, will be distinguished as R_{eo}, W_{eo} and C_{eo} or R_{sp}, W_{sp} and C_{sp}, depending on whether the substitution is carried out for the case of electro-osmosis or of streaming-potential.

It can be proved quite generally that

$$R_{eo} = R_{sp} = R_{cond}$$

but

$$C_{eo} = C_{sp} < C_{cond}.$$

As this general proof requires a rather elaborate mathematical treatment, the analysis given here will be confined to two simple cases, viz. to two capillaries either in parallel or in series. These two cases are completely illustrative of the conditions in a diapraghm, as, apart from cross connections[4]), (which introduce no new features) a diaphragm may be considered as an assembly of capillaries running parallel and/or in series.

The complications arising in the case of combinations of capillaries may be shown qualitatively in the following way.

When two capillaries of *different* diameters are parallel, $v/i = (v_1 + v_2)/(i_1 + i_2)$. If $v_1/i_1 \neq v_2/i_2$, which is realised when surface conductance is present (cf. eq. 2a), v/i acquires some intermediate value. In an experiment on streaming-potentials with the same set of capillaries, E/P would have a different value for each of the capillaries. As the pressure is necessarily the same for both capillaries, the individual values of E would be different, which clearly does not constitute a stationary situation. Consequently an electric current will be generated, in order to compensate the difference between the individual values of the potential difference E, and the final value of E/P will be intermediate between E_1/P_1 and E_2/P_2.

In the case of electro-osmosis through two capillaries in series, the electric current has the same value for both capillaries. As v/i is smaller, the narrower the capillary (cf. eq. 2a) the transport of liquid would be unequal in the two capillaries, which would result in an accumulation or in a flowing-away of the liquid from the junction between the capillaries. Before this happens, however, a pressure difference comes into existence, accelerating the flow of the liquid in the narrower capillary and slackening it in the wider one.

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[4]) A complete analysis, taking account of cross connections as well, will be given in a subsequent paper.

These complications require that we take account of pressure differences in our following analysis of electro-osmosis, and likewise of electric currents in the case of streaming-potentials.

§ 3. *The elementary processes.*

The volume of liquid v_i transported by electro-osmosis through a capillary *i* can be found from Smoluchowski's analysis to be equal to[5])

$$v_i = \frac{\varepsilon\zeta}{4\,\pi\eta} E_iC_i = ZE_iC_i \quad \ldots\ldots\ldots \quad (4)$$

where E_i is the potential difference between the ends of the capillary.

The pressure need not to be a constant throughout the diaphragm and apart from the electro-osmotic transport v_i, a transport of liquid, s_i, under the pressure difference P_i has to be taken into account.

$$s_i = \frac{P_i}{W_i} \quad \ldots\ldots\ldots \quad (5)$$

The convection current caused by the application of an external pressure to the capillary can be taken from the analysis of the streaming potential and is equal to

$$l_i = \frac{\varepsilon\zeta}{4\,\pi\eta} P_iC_i = ZP_iC_i \quad \ldots\ldots\ldots \quad (6)$$

and the conduction current i_i under a potential difference E_i is given by

$$i_i = \frac{E_i}{R_i} \quad \ldots\ldots\ldots \quad (7)$$

Equations (4) and (7) can be combined to form the equation for electro-osmosis

$$\frac{v_i}{i_i} = ZR_iC_i$$

and the equation for the streaming-potential can be derived directly from (6) and (7) by remarking that in the stationary state l_i and i_i must be equal, leading to

$$\frac{E_i}{P_i} = ZR_iC_i$$

It should be remarked, that it is not necessary to take account of the mutual influence of electro-osmosis and streaming-potential[6]). So e.g. in the case of two capillaries in series (vide supra), the extra pressure is important, in so far as it changes the transport of liquid, but the streaming-potential generated by it may be neglected, as this is far smaller than the potential difference applied to produce the electro-osmosis.

§ 4. *Two parallel capillaries.*

Two capillaries, 1 and 2, running parallel can be replaced by a single one in such a way, that all external conditions in the case of *electro-osmosis* remain unaltered. This demands that the transport of liquid through the single

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[5]) In this as in the following equations it has been assumed that the diameter of the capillaries is large compared to the thickness of the double layer.

[6]) At least, if the diameters of the capillaries are larger than a few micra.

capillary is equal to the sum of v_1, v_2, s_1 and s_2, the total current to the sum of i_1 and i_2. The potentials (E_A, E_B) and the pressures (P_A, P_B) in the endpoints A and B should not be altered by the substitution. These conditions are sufficient and necessary to determine the values of R, C, and W for the new capillary, as is demonstrated by the following simple calculation.

$$v_1 = Z(E_A - E_B)C_1 \quad s_1 = \frac{P_A - P_B}{W_1} \quad i_1 = \frac{E_A - E_B}{R_1}$$

$$v_2 = Z(E_A - E_B)C_2 \quad s_2 = \frac{P_A - P_B}{W_2} \quad i_2 = \frac{E_A - E_B}{R_2}$$

$$v + s = v_1 + s_1 + v_2 + s_2 \quad i = i_1 + i_2$$

$$v = Z(E_A - E_B)C_{eo} \quad s = \frac{P_A - P_B}{W_{eo}} \quad i = \frac{E_A - E_B}{R_{eo}}$$

It follows immediately that

$$\frac{1}{R_{eo}} = \frac{1}{R_1} + \frac{1}{R_2}, \quad C_{eo} = C_1 + C_2 \text{ and } \frac{1}{W_{eo}} = \frac{1}{W_1} + \frac{1}{W_2} \quad . \quad . \quad (8)$$

satisfies the conditions, irrespective of the values of the potential and pressure in the junction points, A and B.

An analogous substitution can be carried out for the case of *streaming-potentials*. The conditions are now: the total transport of liquid, s, has to be equal to the sum of s_1 and s_2 and the total transport of electricity being given by $l + i$ has to be equal to the sum of $l_1 + i_1 + l_2 + i_2$.

A simple calculation leads us again to expressions analogous to (8), in which R_{eo}, C_{eo} and W_{eo} have been replaced by R_{sp}, C_{sp} and W_{sp}.

This proves that both the streaming-potential E/P and the electro-osmosis v/i of two parallel capillaries are equal to those of the same single capillary satisfying the conditions (8). Consequently, as this single capillary obeys the normal equations (2 and 3), the equality of E/P and v/i for two parallel capillaries is proved.

A substitution of the two capillaries by a single one for *conductance*, that is a substitution in such a way that the total electric resistance and the capacity of conductance retain their value leads to the conditions

$$\frac{1}{R_{cond}} = \frac{1}{R_1} + \frac{1}{R_2} \qquad C_{cond} = C_1 + C_2$$

As these conditions are identical to those found in (8) one may infer that the application of equation (3) to a system of capillaries running parallel leads to the correct value of ζ.

This would still be true if the surface conductance would have different values for the two capillaries, as the specific surface conductivity has not been used explicitly in our derivations.

§ 5. *Two capillaries in series.*

The replacement of two capillaries AB and BC in series by a single one (AC) offers more difficulties. The substitution for *electro-osmosis* demands that the total transport of liquid, which is equal to $v_1 + s_1 = v_2 + s_2$ remains unchanged. Likewise the new current i has to be equal to $i_1 = i_2$. Pressure and potential in the endpoints A and C must be left uninfluenced.

The calculations are slightly more complicated than in the case of two parallel capillaries, because now the values of the potential and the pressure in B have to be eliminated.

The resulting conditions which the new capillary has to satisfy are found to be

$$W_{eo} = W_1 + W_2 \quad R_{eo} = R_1 + R_2 \text{ and } C_{eo} = \frac{C_1W_1R_1 + C_2W_2R_2}{(W_1 + W_2)(R_1 + R_2)} \quad . \quad (9)$$

The complete calculations leading to (9) are as follows. The condition $i = i_1 = i_2$ leads to

$$\frac{E_A - E_C}{R} = \frac{E_A - E_B}{R_1} = \frac{E_B - E_C}{R_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The condition $v + s = v_1 + s_1 = v_2 + s_2$ leads to

$$Z(E_A - E_C)C + \frac{P_A - P_C}{W} = Z(E_A - E_B)C_1 + \frac{P_A - P_B}{W_1} = Z(E_B - E_C)C_2 + \frac{P_B - P_C}{W_2} \quad . \quad . \quad (11)$$

Elimination of E_B from (10) gives $R = R_1 + R_2$ and elimination of P_B and E_B from (10) and (11) leads to

$$ZCW_1(E_A - E_C) + \frac{W_1}{W}(P_A - P_C) - \frac{ZC_1W_1R_1}{R}(E_A -- E_C) - P_A = P_B =$$

$$= -ZCW_2(E_A - E_C) - \frac{W_2}{W}(P_A - P_C) + \frac{ZC_2W_2R_2}{R}(E_A - E_C) - P_C$$

or, if again $(E_A - E_C)$ and $(P_A - P_C)$ are considered to be independent variables
$W = W_1 + W_2$ and $CWR = C_1W_1R_1 + C_2W_2R_2$

The substitution for *streaming-potentials,* demanding again constancy of transport of liquid and of electricity or $s = s_1 = s_2$ and $l + i = l_1 + i_1 = l_2 + i_2$, leads to the same conditions (9) already found for electro-osmosis.

The substitution for *conductance,* however, demanding constancy of resistance and of capacity of conductance leads to the same condition for R but to a deviating condition for C viz.

$$R_{cond} = R_1 + R_2 \text{ and } \frac{1}{C_{cond}} = \frac{1}{C_1} + \frac{1}{C_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The fact that the substitutions for electro-osmosis and for streaming-potentials are identical proves that also in the case of capillaries in series the values of E/P and v/i are equal under all circumstances of conductivity. But the fact that according to (12) and (9) C_{cond} has another value than $C_{eo} = C_{sp}$ frustrates a direct application of (3) to the case of capillaries in series since it leads to erroneous values of ζ.

The exact value of ζ can be found in this case by the application of (3) to the single capillary obeying the conditions (9) or

$$\frac{E}{P} = \frac{v}{i} = \frac{\varepsilon\zeta}{4\,\pi\eta} R_{eo} C_{eo} = \frac{\varepsilon\zeta}{4\,\pi\eta} \frac{C_1W_1R_1 + C_2W_2R_2}{W_1 + W_2} \quad . \quad . \quad . \quad (13)$$

The direct application of (3) to the system of the two capillaries in series would have resulted in

$$\frac{E}{P} = \frac{v}{i} = \frac{\varepsilon\zeta'}{4\,\pi\eta} R_{cond}C_{cond} = \frac{\varepsilon\zeta'}{4\,\pi\eta} \frac{R_1 + R_2}{1/C_1 + 1/C_2} \quad . \quad . \quad . \quad . \quad (14)$$

Thus the ratio of the erroneous value of ζ' to the exact ζ is

$$\frac{\zeta'}{\zeta} = \frac{(C_1W_1R_1 + C_2W_2R_2)(1/C_1 + 1/C_2)}{(R_1 + R_2)(W_1 + W_2)} \quad \ldots\ldots \quad (15)$$

When surface conductance is absent this proportion is equal to 1 as is easily verified.

When however the surface conductance is preponderant, so that R is proportional to l/r instead of to l/r^2 the ratio of ζ' to ζ becomes (l_i and r_i are length and radius of the individual capillaries)

$$\frac{\zeta'}{\zeta} = \frac{\Sigma l_i/r_i{}^3 \,.\, \Sigma l_i/r_i{}^2}{\Sigma l_i/r_i{}^4 \,.\, \Sigma l_i/r_i} \quad \ldots\ldots \quad (16)$$

and this proportion is always smaller than 1.

Equation (16) may be generalized to the case of a large number of short capillaries (length dl, radius r) leading to

$$\frac{\zeta'}{\zeta} = \frac{\int \frac{1}{r^3}\,dl \int \frac{1}{r^2}\,dl}{\int \frac{1}{r^4}\,dl \int \frac{1}{r}\,dl} = \frac{\overline{1/r^3} \,.\, \overline{1/r^2}}{\overline{1/r^4} \,.\, \overline{1/r}} < 1$$

If the individual values of 1/r for pieces of the capillary of equal length are denoted by a, b, c, ... the ratio

$$\frac{\overline{1/r^2} \,.\, \overline{1/r^3}}{\overline{1/r^2} \,.\, \overline{1/r}} = \frac{(a^2 + b^2 + c^2 \ldots)(a^3 + b^3 + c^3 \ldots)}{(a^4 + b^4 + c^4 \ldots)(a + b + c \ldots)}$$

may be converted into

$$\frac{a^5 + b^5 + \ldots\ldots + ab(a + b)ab + \ldots\ldots}{a^5 + b^5 + \ldots\ldots + ab(a + b)(a^2 - ab + b^2) \ldots\ldots}$$

and as always

$$ab < a^2 - ab + b^2$$

the ratio

$$\frac{\overline{1/r^2} \,.\, \overline{1/r^3}}{\overline{1/r^4} \,.\, \overline{1/r}} < 1.$$

The depression of ζ calculated in the wrong way can be very considerable as is shown by the following numerical examples.

$$\begin{array}{lll} l_1 = 15\, l_2 & r_1 = 3\, r_2 & \zeta'/\zeta = 7/12 \\ l_1 = 32\, l_2 & r_1 = 4\, r_2 & \zeta'/\zeta = 4/9 \\ l_1 = 243\, l_2 & r_1 = 9\, r_2 & \zeta'/\zeta = 9/49 \sim 1/5! \end{array}$$

§ 6. *Conclusions.*

As the substitution of a network of capillaries by a single capillary can always be carried out, and as this substitution is identical for electro-osmosis and for streaming-potential, the values of E/P and v/i are identical for any diaphragm, even in the presence of considerable surface conductance. In the foregoing sections this has been proved for some typical cases. At the same time this constitutes a proof, that a diaphragm, consisting of an arbitrary number of capillaries connected in series and/or in parallel, shows equal values of streaming-potential and electro-osmosis. By a repeated application of the substitutions treated in sections 4 and 5, such a diaphragm may indeed be reduced to a single capillary, for which E/P = v/i.

If these values of E/P and v/i, however, are interpreted in the usual way on the basis of equation (2b) or (3) the ζ-potential thus found is *too low* on account of the fact that in the diaphragm capillaries of different diameters are connected in series with each other, which is inevitable if the diaphragm is built up from granular material. The amount of the depression increases with increasing importance of surface conductivity, that is with increasing dilution of the solutions. The procentual error in ζ goes to a limit when the surface conductance outweighs the bulk conductance completely. This limit depends on the structure of the diaphragm.

Unfortunately it is not possible to indicate the exact value of the necessary correction without a more precise knowledge of the structure of the diaphragm. This knowledge can not be obtained by measurements of the hydrodynamic resistance (W), the electric resistance (R) or the capacity of conductance (C) of the diaphragm.

So long as the theoretical situation is not ameliorated, evaluation of ζ-potentials from measurements with diaphragms showing surface conductance should be mistrusted.

Results confirming this can be found in the thesis of one of us [7]), where the ζ evaluated from diaphragms of powdered glass is found to be 70 mV against 140 mV for a capillary of the same glass, when the liquid is conductivity water, whereas the two values are 98 mV and 112 mV for 2.10^{-4} *n* KNO_3.

Eindhoven, *Natuurkundig Laboratorium der N.V. Philips' Gloeilampenfabrieken.*
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[7]) P. W. O. Wijga, Thesis Utrecht 1946.