Theoretical bases of electro-osmotic phenomenon

W. SCHAAD

I. – INTRODUCTION

The application of electrokinetic phenomena in foundation and civil engineering has increased since a period of ten years and new procedures have been established and applicated in practice. Regarding the literature, only little progress in fundamental researches has been published. Often the publications are repetitions of the known facts or represent partial research without considering the basic laws, as already stated by L. Casagrande (1) (*). Considering the development of theories on electrosmotic groundwater flow there may be seen that starting from the Helmholtz theory, the general basic laws developed by the author and R. Haefeli were published already in 1946-1948 (2-5):

$$v_F = k \cdot J_h + k_e \cdot E \qquad [1]$$

$$\vec{v}_F = -\mathrm{grad}\ (k \cdot \varnothing_H + k_e \cdot \varnothing_E) \qquad [2]$$

$$k \cdot \Delta\varnothing_H + D_B \cdot \Delta\varnothing_E = -4\pi\varepsilon \qquad [3]$$

(valid in C.G.S.–System)

as well as approximative formulas for computing electrosmotic filter-well systems. In the equations 1-3 the symbols mean the following magnitudes:

v_F = total filter speed
k = hydraulic permeability coefficient (Darcy)
k_e = electrosmotic permeability coefficient
J_h = hydraulic gradient
E = electric field strength (electric potential gradient)
$\varnothing_H$ = hydraulic potential
$\varnothing_E$ = electric potential
D_B = dielectric constant of soil
ε = electrical charge density of the space unit

In 1949 L. Casagrande published a similar theory, practically the same, but renouncing to the treatment of the above general laws for electrosmotic flow in porous media (6). The differential equation [3] shows by its Laplacian character, that the electrosmotic phenomena base on similar potential field laws like apparented phenomena:

thermic phenomena, heat transmission
electric phenomena
groundwater flow
elastic phenomena

and that solutions of problems with similar boundary conditions in these dominions may be transformed to problems of electrosmotic flow. Only little use of these relations has been made e.g. by Winterkorn treating questions of this character (7) (*).

In former publications the author mentioned, that since the establishment of the Helmholtz theory discussions and contradictory views arised and that these questions never were solved. Further the application of this theory reaches certain limits, where the hypothesis of Helmholtz is no more valid and leads to results contradictory to observation. It may be briefly stated, that for all problems dealing with the influence of diameter of capillaries these contradictions appear decisive.

(*) The numbers refer to the references at the end of the paper.

(*) After the accomplishment of the manuscript diverse publications have appeared representing remarkable steps in the development of electro-osmotic base research. [16-19].

In the succeeding parts, the following symbols are used:

Symbols

a = radius of capillary
a_{M_E} = ions activity of chemical solutions
c = concentration of chemical solutions
C = coefficient of double layer effect
d = diameter of capillary
D = dielectric constant of liquid (water)
D_B = dielectric constant of soil
e = electric charge
E = electric field strength
f = area, cross section of capillary
f_a = activity coefficient of chemical solutions
F = area, cross section
j_c = density of electric current of capillary (medium density)
j_q = density of electrolytic current
j_ω = density of electrosmotic current
J_h = hydraulic gradient
J = current strength
J_q = electrolytic current strength
J_ω = electrosmotic current strength
k = coefficient of hydraulic permeability (Darcy)
k_e = coefficient of electrosmotic permeability
K = active force
K' = passive force
l = length of capillary
n = porosity
Q = discharge
r = radius
R_o = gas constant
R_ω = electric surface resistance
R_q = electric resistance (Ohm)
t = time
T = temperature
T_a = absolute temperature
U = potential difference (voltage)
u = flow velocity
u_c = electrosmotic speed in capillary (medium speed)
u_ω = electrosmotic speed of boundary layer
v_e = electrosmotic filter speed
v_F = hydraulic filter speed
x = variable length
z = sliding constant (Lamb)
α_e = ratio of electrosmotic and electrolytic current
β = friction coefficient (Lamb)
β_e = coefficient of electrosmotic action
δ = thickness of double layer
ε = electrical charge density
ζ = elektrokinetic particle potential (Helmholtz)
η = viscosity
$\varkappa$ = ratio of elektrokinetic particle potentials
λ = transformation factor
ξ = modified electrokinetic particle potential
ρ = specific electric resistance
ϱ_L = specific electric resistance of liquid
ϱ_ω = specific electric resistance of surface conduction
τ = shearing resistance
φ = potential of boundary layer
φ_a = potential of outer face of boundary layer
φ_i = potential of inner face of boundary layer
$\Delta\varphi$ = potential difference
$\Delta\varphi_o$ = normal potential against normal hydrogen electrode
$\O_E$ = electric potential
$\O_H$ = hydraulic potential.

II. – Classic bases of electrosmotic flow

For the following deductions the determining points of the diverse types of hypothesis will be outlined:

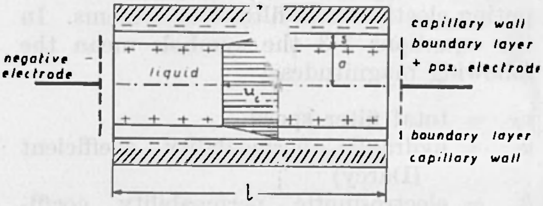

Fig. 1. – Capillary conditions of electrosmotic flow, according to Helmholtz

a) *Helmholtz's Hypothesis*: *Fig. 1*

1) Besides other assumptions Helmholtz(8) supposes, that within a thin boundary film

the velocity of liquid increases from zero on the wall to the maximum u_c.

2) The intensity of electric current is uniformly distributed on the whole section of capillary.

3) Within the interior of the capillary section the particles of liquid are transported with the above speed u_c.

These assumptions lead to the well known law of electrosmotic capillary speed, which is valid for C.G.S.-system and normally serves as a theoretical basis for considerations of the electrosmotic coefficient of permeability k_e:

$$u_c = \zeta \frac{\varrho_L \cdot D}{4\,\pi\eta} \cdot j_c = \zeta \frac{D}{4\,\pi\eta} \cdot E \qquad [4]$$

wherein:

u_c — medium electrosmotic speed in capillary
ζ = electrokinetic particle potential
ϱ_L = specific electric resistance of liquid
D = dielectric constant of liquid phase
η = viscosity of the liquid
j_c = electrical current density in the capillary
E = electrical field strength.

b) *Lamb's hypothesis*

Lamb considers the boundary film as an electric double layer of thickness δ, where the inner layer displaces relatively to the fix outer layer under the action of electrical forces (⁹). He introduces a friction coefficient β between the two layers and obtains (when transformed to the Helmholtz expressions):

$$u_c = \zeta \cdot \frac{\varrho_L \cdot D}{4\,\pi \cdot \delta \cdot \beta} \cdot j_c \cdot \qquad [5]$$

When β is transformed to $\frac{\eta}{z}$, wherein η means the viscosity, z a sliding constant, the following expression is obtained

$$u_c = \zeta \frac{\varrho_L \cdot D}{4\,\pi\eta} \cdot \frac{z}{\delta} \cdot j_c \cdot \qquad [6]$$

The result gives a formula similar to the Helmholtz law, but with a constant factor $\frac{z}{\delta}$. In the case of $z = \delta$ the two laws are identical. One may easily show, that this holds for assuming laminar flow (opposite to the point of view of Lamb) within the boundary layer.

c) *Perrin's hypothesis.*

In the first period of the development of basic knowledge of electrosmotic flow the deductions of Perrin gave one of the most important advances showing the relation between electrosmosis and physical chemistry (¹⁰). His physical conception on electrosmotic flow is practically the same as the Helmholtz hypothesis. But his deduction of the law gives the most elegant and simplest way of derivation and was determining for the considerations of this paper.

Perrin considers the double layer as an electric condenser with a certain capacity, a most useful conception for deduction (Fig. 2).

The conception of Perrin is the following one:

If in the moving part of the double layer the unit density of electric charges is ε and E the electric field strength, the active unit force on moving layer is $\varepsilon \cdot E$ and assuming laminar flow within the layer of thickness δ the passive force is $\eta \cdot \frac{u_c}{\delta}$ therefore:

$$\varepsilon \cdot E = \eta \frac{u_c}{\delta} \qquad [7]$$

$$u_c = \frac{\varepsilon \cdot E}{\eta} \cdot \delta \qquad [8]$$

Considering the double layer as a condenser the difference of potential $(\varphi_i - \varphi_a) = \zeta$ of the double layer is obtained (E_δ being the electric field strength of double layer)

$$\zeta = E_\delta \cdot \delta = \frac{4\,\pi\varepsilon}{D} \cdot \delta \qquad [9]$$

$$\varepsilon = \frac{\zeta \cdot D}{4\,\pi\delta}\ ; \qquad [10]$$

introduced in eq. [8]

$$u_c = \zeta \frac{D}{4\,\pi\eta} \cdot E\,. \qquad [11]$$

Introducing $E = \varrho_L \cdot j_c$ the electrokinetic speed becomes:

$$u_c = \zeta \frac{\varrho_L \cdot D}{4\,\pi\eta} \cdot j_c\,. \qquad [12]$$

according to the Helmholtz formula [4].

Further Perrin has introduced the relation between the ζ-potential and concentration of the liquid. This relation follows in a modern form (11), taking in consideration the advances of physical chemistry since the time of Perrin. If $\Delta\varphi$ designates the potential difference of a metal against its solution with the ions activity:

$$a_{M_E} = f_a \cdot c \qquad [13]$$

where f_a means the activity coefficient and c the concentration of the solution in Mol/Liter the potential difference becomes:

$$\Delta\varphi = \Delta\varphi_o + 0.277 + \frac{R_o\,T_a}{n \cdot F}\, ln\, a_{M_E} \text{ volts} \qquad [14]$$

where:

$\Delta\varphi_o$ = normal potential against normal hydrogen electrode

R_o = gas constant = 8,31 Joule/Grad

T_a = absolute temperature

n = valence of the ions

F = constant of Faradays law = $= 96.500 \dfrac{\text{Amp} \cdot \text{sec}}{\text{Mol (valence 1)}}$.

For concentration less than $1/100 \dfrac{\text{Mol}}{\text{Lit}}$ the activity coefficient f_a is

$$f_a = 1 - 1.15 \sqrt{c}\,. \qquad [15]$$

The following table 1 contains the normal potentials of diverse elements as well as the absolute potentials (ions activity $a_{M_E} = 1$).

Table 1. — NORMAL AND ABSOLUTE POTENTIALS (from ref. 11)

Element	Normal potential Volt	Absolute potential Volt
Li	— 3.02	— 2.743
K	— 2.92	— 2.643
Na	— 2.71	— 2.433
Al	— 1.28	— 1.003
Mn	— 1.08	— 0.803
Zn	— 0.758	— 0.481
Fe	— 0.43	— 0.153
Pb	— 0.12	+ 0.157
H_2	0	+ 0.277
Cu	+ 0.345	+ 0.622
Ag	+ 0.80	+ 1.077

The relation between the electrokinetic particle potential and the above galvanic potential difference will be discussed later.

Comparing all the diverse types of hypothesis, the conceptions are in general equivalent with little deviations, hence the result is practically the same for all these classic theories. Assuming laminar flow, the same electrosmotic speed u_c in a capillary results from these deductions.

III. - RELATION BETWEEN CLASSIC LAWS AND ELECTROSMOTIC FILTER LAW FOR DIAPHRAGMS

In the authors formula [1] the electrosmotic filter speed v_e is given by

$$v_e = k_e \cdot E\,. \qquad [16]$$

Comparing the formula [4]

$$u_c = \zeta \cdot \frac{\varrho_L \cdot D}{4\,\pi\eta} \cdot j_c = \zeta \cdot \frac{D}{4\,\pi\eta} \cdot E \qquad [4]$$

with the above expression [16], a transformation is needed. Since the formula [4] is only valid for the C.G.S.-system and expression [1] respectively [16] for practical system, a transformation factor λ must be introduced. The relations between practical and C.G.S. units are given in table 2:

Table 2. — TRANSFORMATION OF PHYSICAL UNITS

Magnitudes	Practical units	C.G.S. units
ζ	1 Volt	$= \frac{1}{300}$ U.C.G.S.
ϱ_L	1 Ohm cm	$= \frac{1}{9} \cdot 10^{-11}$ »
j_c	1 Amp/cm²	$= 3 . 10^{9}$ »
η	1 g*cm⁻² sec	$= 981$ »

With these relations the electrosmotic capillary speed follows for technical uses:

$$u_c = \lambda \cdot \zeta \cdot \frac{\varrho_L \cdot D}{4 \pi \eta} \cdot j_c \text{ cm/sec} \qquad [17]$$

wherein

$$\lambda = \frac{\frac{1}{300} \cdot \frac{1}{9} \cdot 10^{-11} \cdot 3 \cdot 10^{9}}{981} =$$

$$= 1{,}13 \cdot 10^{-8} \, .$$

Introducing $E = \varrho_L \cdot j_c$ the expression obtained is:

$$u_c = \lambda \cdot \zeta \cdot \frac{D}{4 \pi \eta} \cdot E \qquad [18]$$

(electrosmotic capillary speed).

Idealizing a porous medium as a capillary bundle with the section of capillary $f = \pi \cdot a^2$, the total section F (filter section) and N the number of capillaries within the section F, the electrosmotic filter speed v_e is obtained:

$$v_e = \frac{N \cdot f}{F} \cdot u_c = n \cdot \lambda \cdot \zeta \cdot \frac{D}{4 \pi \eta} \cdot E \qquad [19]$$

wherein n designates the porosity of the diaphragm. Comparing expression [19] with expression

$$v_e = k_e \cdot E \qquad [16]$$

we obtain:

$$k_e = \lambda \cdot n \cdot \zeta \frac{D}{4 \pi \eta} \qquad [20]$$

From the following table 3 may be seen that the electrosmotic particle potential ζ normally varies within narrow limits of the order of magnitude of 10^{-2} Volts

Table 3. — ELECTROKINETIC PARTICLE POTENTIALS OF DIVERSE SUBSTANCES (from ref. 13)

Liquid	Substance	Particle diameter	Temps.	Electrock. part. pot. Volt	Investigators
water	quartz	1μ	—	0.044	Whitney a. Blake 1904
»	glass	—	—	0.052-0.053	Dorn 1879-1880
»	Au	$< 0.1\mu$	—	0.058	Whitney a. Blake 1904
»	»	»	18°	0.032	Burton 1906
»	»	»	18°	0.048	Burton 1906
»	Ag	»	—	0.048	Cotton a. Mouton
»	»	»	18°	0.034	Burton 1906
»	»	»	18°	0.032	Burton 1906
»	Pt	»	—	0.044	Whitney a. Blake 1904
»	»	»	18°	0.030	Burton 1906
»	$Fe(OH)_2$	»	—	-0.044	Whitney a. Blake 1904
»	$Cu(OH)_2$	»	18°	-0.048	Burton 1909
»	Oils	2μ	25°	0.063	Ridsdale Ellis 1911

The dielectric constant D of water is 80, and the viscosity of water:

$$\eta = \frac{0{,}00001814}{1 + 0{,}0337 \cdot T + 0{,}00022 \cdot T^2} \; g^* \, \mathrm{cm}^{-2} \, \mathrm{sec} \qquad [21]$$

T — temperature in °Cels.

For checking the order of k_e the porosity n is introduced for the practical range of soils:

$$n = 20 \div 30\% \text{ and}$$

$$\eta_{4^\circ} = 1{,}595 \cdot 10^{-5} \; g^* \, \mathrm{cm}^{-2} \, \mathrm{sec}$$

Taking for ζ the value of quartz from table 3: $\zeta = 0{,}044$ Volt, the theoretical value of quartz powder is obtained:

$$k_e = 1{,}13 \cdot 10^{-8} (0{,}2 \div 0{,}3) \cdot \frac{4{,}4 \cdot 10^{-2} \cdot 80}{4 \, \pi \cdot 1{,}595 \cdot 10^{-5}}$$

$$k_e \simeq (4{,}0 \div 6{,}0) . 10^{-5} \, \frac{\mathrm{cm/sec}}{\mathrm{Volt/cm}} \; .$$

This result agrees very well with the values k_e determined for quartz powders (table 4):

Table 4. — COEFFICIENT OF ELECTROSMOTIC PERMEABILITY FOR QUARTZ POWDERS

Investigator	$10^5 . k_e$ in $\frac{\mathrm{cm/sec}}{\mathrm{Volt/cm}}$
Leo Casagrande	4,3
Bernatzik	6,8
Schaad-Haefeli	4,5
Schaad (range of numerous test series)	2,5 ÷ 5,2

With these deduction, the relation between the theory of Helmholtz-Lamb-Perrin of electrosmotic capillary flow and the electrosmotic filter speed according to expressions [1] and [16] is given.

In normal cases of practical application the expression [19] is sufficient, i.e. for the determination of the flow velocity of liquid, where the diameter of the capillaries does not influence the results and the electrosmotic discharge of solution is independent from this magnitude.

In the cases of theoretic developments based on the classic theory, e.g. for the electrosmotic rise in function of the capillary diameter, contradictions of theoretic results appear showing, that the classic theory is no more sufficient for these deductions concerned. On the opposite, the filter laws lead to satisfactory results.

The author briefly mentioned these contradictions in 1948 (^{12}), but no clear solution was available in that time. In the meanwhile these problems have been cleared up more and will be outlined in the following chapters.

IV. – Contradictions of classic laws

Observance of the boundary conditions.

Regarding expression [4]

$$u_c = \zeta \cdot \frac{D}{4 \, \pi \eta} \cdot E \qquad (\mathrm{C.G.S.}) \qquad [4]$$

the electrosmotic discharge of a capillary Q is expressed by:

$$Q = \zeta \cdot \frac{\pi \, a^2 \cdot D}{4 \, \pi \eta} \cdot E = \zeta \cdot \frac{a^2 \cdot D}{4 \, \eta} \cdot E \; . \qquad [22]$$

This result would mean, that the other magnitudes being constant the discharge Q would increase in a quadratic function of he capillary diameter $d = 2a$.

For an infinite diameter Q would be infinite and for a diameter of d = zero the discharge would be zero. On the other hand the potential is obtained $\zeta \sim \frac{1}{a^2}$ if the other magnitudes are kept constant.

The experience shows in contrast to these theoretic deduction, that the discharge reaches an upper limit of diameter d, where a measurable discharge can no more be observed.

On the opposite fine-grained materials like bentonite and even gelatine gels may show the same or even higher discharges than coarser materials like quartz powders and silts e.g.:

Table 5. — ELECTROSMOTIC PERMEABILITY COEFFICIENTS OF BENTONITE AND GELATINE

Material	$10^5 k_e \frac{\text{cm/sec}}{\text{Volt/cm}}$
Na-Bentonite	2-12 (Leo Casagrande)
Gelatine gel	5 (» »)

Refering to expression [20] the experience shows that k_e generally varies within narrow limits. Its order of magnitude is more or less independent of the soil type. Additionally regarded the definition of ζ-potential of a double layer, it is not visible, why thisone should depend on other geometrie magnitudes of the capillary diaphragm, like a or n, than on the thickness δ of double layer. The character of ζ-potential being decisive for diverse problems this question will be outlined in a more detailed form.

V. – NATURE OF THE ELECTROKINETIC PARTICLE POTENTIAL (Fig. 2).

Using Perrins conception, regarding the electric double layer as an electric condenser (Fig. 2) the field strength of the layer $E\delta$ is:

$$E = \frac{\Delta\varphi}{\delta} = \frac{4\pi e}{F \cdot D} \quad \text{(C.G.S.)} \qquad [23]$$

when $\Delta\varphi$ is the potential difference $(\varphi_i - \varphi_a)$, F the layer surface and e the charge of double layer.

The surface being:

$$F = 2\pi a \cdot l \qquad [24]$$

we obtain:

$$\Delta\varphi = \frac{4\pi e}{D} \cdot \frac{\delta}{2\pi a \cdot l} = \frac{2e}{D} \cdot \frac{\delta}{a \cdot l} \qquad [25]$$

due to its definition $\Delta\varphi$ is identical with the electrokinetic particle potential ζ. hence

$$\zeta = \frac{2}{D} \cdot \frac{e}{l} \cdot \frac{\delta}{a} \qquad [26]$$

The charge per unit length of the capillary being given by

$$\frac{e}{l} = \zeta \cdot \frac{D}{2} \cdot \frac{a}{\delta} \qquad [27]$$

the unit force K exerted by the electric field strength E results:

$$K = E \cdot \frac{e}{l} = \zeta \cdot \frac{D\,a}{2\,\delta} \cdot E$$

$$K = \zeta \cdot \frac{D \cdot a}{2\,\delta} \cdot \varrho_L \cdot j_c \,. \qquad [28]$$

On the other hand the friction force K' of laminar flow is expressed by:

$$K' = \eta \cdot \frac{du}{dr} \cdot 2\pi r \qquad [29]$$

if r is any radius between zero and a. For the double layer

$$r = a \quad \text{and} \quad \frac{du}{dr} = \frac{u_c}{\delta},$$

the friction force becomes:

$$K' = \eta \cdot \frac{u_c}{\delta} \cdot 2\pi a \,. \qquad [30]$$

In the case of stationary flow we obtain $K = K'$:

$$[28, 30] \quad \zeta \cdot \frac{D \cdot a}{2 \cdot \delta} \cdot \varrho_L j_c = \eta \cdot \frac{u_c}{\delta} \cdot 2\pi a$$

$$4) \quad u_c = \zeta \, \frac{\varrho_L \cdot D}{4\,\pi\,\eta} \cdot j_c$$

the Helmholtz formula.

Introducing now the ζ-potential from expression [26] into [4], there results:

$$u_c = \frac{2e}{D} \cdot \frac{\delta}{a \cdot l} \cdot \frac{\varrho_L \cdot D}{4\pi\eta} \cdot j_c =$$

$$= \frac{e}{l} \cdot \frac{\delta}{a} \cdot \frac{\varrho_L}{2\pi\eta} \cdot j_c$$

since

$$j_c = \frac{J}{F}, \; J = \frac{de}{dt}, \qquad (t = \text{time})$$

$$j_c = \frac{1}{F} \frac{de}{dt}$$

$$F = \pi \cdot a^2 \qquad [31]$$

we obtain:

$$u_c = \frac{e}{l} \frac{\delta}{a} \frac{\varrho_L}{2\pi\eta} \frac{1}{\pi a^2} \cdot \frac{de}{dt} =$$

$$= \frac{\delta}{2a^3 l} \cdot \frac{\varrho_L}{\pi^2 \cdot \eta} \cdot e \cdot \frac{de}{dt}. \qquad [32]$$

If x designates the way of a particle situated in the boundary layer and t the time, the speed u_c is found:

$$u_c = \frac{dx}{dt} \qquad [33]$$

introduced in [32]

$$dx = \frac{\delta}{2 \cdot a^3 \cdot l} \cdot \frac{\varrho_L}{\pi^2 \cdot \eta} \cdot e \cdot de. \qquad [34]$$

By integration within the limits $x = o \rightarrow l$ according to $e = o \rightarrow e$ we find:

$$\int_o^l dx = \frac{\delta}{2a^3 l} \cdot \frac{\varrho_L}{\pi^2 \cdot \eta} \int_o^e e \cdot de$$

$$l = \frac{\delta}{2a^3 l} \cdot \frac{\varrho_L}{\pi^2 \cdot \eta} \cdot \frac{e^2}{2}$$

$$e^2 = \frac{4a^3 \pi^2}{\delta \cdot \varrho_L} \cdot l^2 \cdot \eta \qquad [35]$$

and the electric charge of double layer becomes:

$$e = 2 a \pi \sqrt{\frac{a \cdot \eta}{\delta \cdot \varrho_L}} \cdot l \qquad [36]$$

respectively the charge per unit length:

$$\frac{e}{l} = 2 a \pi \sqrt{\frac{a \cdot \eta}{\delta \cdot \varrho_L}}. \qquad [37]$$

Introducing this value in expression [26] the ζ-potential is obtained:

$$\zeta = \frac{4a \cdot \pi}{D} \cdot \frac{\delta}{a} \cdot \sqrt{\frac{a \cdot \eta}{\delta \cdot \varrho_L}} =$$

$$= \frac{4\pi}{D} \sqrt{\frac{a \cdot \delta \cdot \eta}{\varrho_L}}. \qquad [38]$$

Further combining expression [37] with [31] the electrosmotic capillary speed u_c is obtained:

$$u_c = 2 a \pi \cdot \sqrt{\frac{a \cdot \eta}{\delta \cdot \varrho_L}} \cdot \frac{\delta}{a} \cdot \frac{\varrho_L}{2\pi\eta} \cdot j_c \qquad [39]$$

$$u_c = \sqrt{\frac{\delta \cdot a \cdot \varrho_L}{\eta}} \cdot j_c \qquad [40]$$

modified Helmholtz formula respectively with $j_c = \frac{E}{\varrho_L}$

$$u_c = \sqrt{\frac{\delta \cdot a}{\varrho_L \cdot \eta}} \cdot E. \qquad [41]$$

From combination of the expressions [41] and [4] results:

$$\zeta \frac{D}{4\pi\eta} = \sqrt{\frac{\delta \cdot a}{\varrho_L \cdot \eta}}. \qquad [42]$$

All these formulas are only valid for C.G.S.-system. For obtaining the value of eq. [42] in practical units, we have to transform with the former factor $n . \lambda$ and obtain:

$$k_e = n . \lambda \cdot \zeta \cdot \frac{D}{4\pi\eta} = n\lambda \sqrt{\frac{\delta . a}{\varrho_L \cdot \eta}} \qquad [43]$$

valid in practical system.

All the results given by expression [38-43] are based on the classic assumptions, especially on the assumption, that the electric current is uniformly distributed over the section of capillary. With regard to the transport of ions this hypothesis must be called in question.

Further the classic theory neglects completely an important factor, the galvanic transport of ions within the interior of the capillary i.e. electrolysis. This phenomenon takes place parallely to electrosmosis and transport of electric charges is caused by both parts. The galvanic current causes electrolysis of the liquid, a phenomenon, that is well known, and the transport within the double layer creates another type, a superficial electric current, we will call it electrosmotic current.

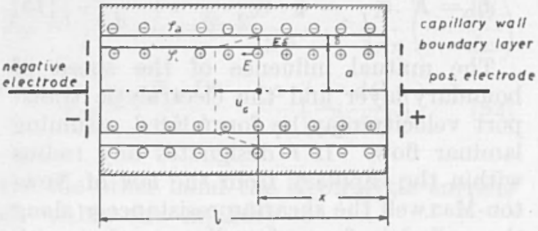

Fig. 2. – Electrosmotic action of capillary, according to Perrin

Regarding the ζ-potential in the form of equation [38] this-one would depend on a geometric magnitude outside the double layer, the capillary radius a. Since this-one is normally much greater than the thickness δ of double layer, there is no reason for the fact, that the interface potential should depend on the radius of the capillary. Furthermore the ζ–potentials determined on the basis of the classic theory show an order of magnitude of 10^{-2} volts (table 3) in contrast to the contact potentials of galvanic chains, that normally show orders of volts. The character of these potentials is the same one. Therefore the question of the cause of this difference of magnitude of potential differences

$$\varDelta\varphi = \zeta \qquad \text{arises.}$$

Furthermore this type of formulas deduced, if really valid, would give the relations between physical constants and the ζ–potential and allow to determine the thickness δ of the double layer, further procure a more detailed knowledge of the electrosmotic permeability coefficient k_e. For diverse practical problems this relation is very important.

The author seeked to solve this problem since his beginning of the research in the dominion of electrosmotic phenomena. Since these questions are related to capillary physics and physical chemistry, they are strange for a civil engineer and would better be treated by colleagues of physical disciplines more suited for the present type of questions.

Not having found a physicist or chemist orientated on the theory of electrosmosis as well as in the field of its practical applications in civil engineering the author decided to treat the questions himself and the necessary studies in electro-physics were undertaken.

The study has lead to a hypothesis, that accords better to the boundary conditions and removes the stated contradictions. A scientific proof of the following theory was only possible by physical reflexions. For an experimental judgement the direct measurement of the ζ-potential would be necessary, a very difficult problem. For this purpose the potential differences between nonconductors and aqueous solutions would have to be determined.

VI. – MECHANICS OF ELECTRIC CHARGES TRANSPORT IN CAPILLARIES UNDER THE ACTION OF AN ELECTRIC FIELD.

For the following deduction we will idealise as usual a porous diaphragm as a bundle of capillaries. The solid particles shall consist of non-conductive material. The theory can easily be enlarged on conductive material, but the mathematical treatment is burdened with more complicated terms, what is not necessary for the principal general questions and the application to soil mechanics.

In the capillary laminar flow is assumed. Besides, the same assumptions are made as in the classic theory, except the distribution of flow velocity. The electrokinetic particle potential is defined in the same manner as the potential difference $\varDelta\varphi = \varphi_i - \varphi_a$, but it will be designated with ξ. since it shows an other order of magnitude than the electrosmotic particle potential ζ according to Helmholtz.

Considering a capillary (Fig. 3) filled with an aqueous solution and under the action of an electric potential difference U with the electric field strength $E = \dfrac{U}{l}$, on the one hand the dissociated ions of the solution move in both directions under the action of field strength E. The positive particles wander from the anode to the cathode and inversely the negative ones from the cathode to the anode. This phenomenon is called electrolysis and follows the law of Faraday. The transport of the ions causes the electrolytic current J_q in the interior of the capillary.

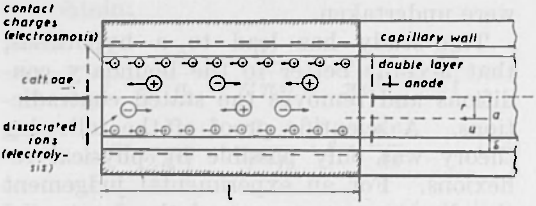

Fig. 3. – Distribution and direction of electric charges flow of aqueous solution under the action of an electric field.

On the other hand in the contact surface between the wall and the solution a double layer is formed according to the classic theory.

For the following considerations the thickness δ of the double layer is very small in proportion to the radius a of the capillary.

Under the action of the electric field the charged particles of the double layer normally move from the anode to the cathode causing too a continuous transport of electric charges i.e. an electric surface current J_ω.

Both currents are present at the same time and both phenomena appear in combination.

According to Perrin's conception the boundary layer shall now be regarded as an electric condenser. In equation [25] the potential difference of the double layer has already been determined:

$$\Delta\varphi = \frac{2e}{D} \cdot \frac{\delta}{a \cdot l} = \xi \qquad [25]$$

and the charge of unit length of the capillary results:

$$\frac{e}{l} = \xi \cdot \frac{D \cdot a}{2\,\delta} \cdot \qquad [44]$$

Under the action of field strength $E = -\frac{d\emptyset_E}{a\,x}$. where $\emptyset_E$ designates the active, electric potential in direction of flow, the active force K per unit length of the positive layer is represented by:

$$K = E \cdot \frac{e}{l} = \xi \cdot \frac{D \cdot a}{2 \cdot \delta} \cdot \left(-\frac{d\emptyset_E}{dx}\right) \qquad [45]$$

The mutual influence of the speed of boundary layer and the electrolytic transport velocity may be formulated assuming laminar flow. If r designates any radius within the capillary from the law of Newton-Maxwell the shearing resistance τ along the cylindric face of radius moving with the speed u within the liquid phase is found

$$\tau = \eta \cdot \frac{du}{dr} \qquad [46]$$

and the passive force K' per unit length acting on this cylinder is obtained

$$K' = 2\,\pi r \cdot \tau = 2\pi\eta \cdot r \cdot \frac{du}{dr} \cdot \qquad [47]$$

For the radius a of capillary the velocity of double layer is u_ω and its gradient within the double layer of thickness δ

$$\frac{du}{dr} = \frac{u_\omega}{\delta} \cdot \qquad [48]$$

Hence the passive force is obtained

$$K' = 2\pi a \cdot \eta \cdot \frac{u_\omega}{\delta} \cdot \qquad [49]$$

The condition of stationary permanent flow furnishes:

$$K = K' \qquad [50]$$

and by introducing this condition in eq. [45] and [49]

$$K = \xi \cdot \frac{D \cdot a}{2\,\delta} \cdot \left(-\frac{d\emptyset}{dx}\right) = 2\,\pi\,a\,\eta \cdot \frac{u_\omega}{\delta} = K'$$

$$u_\omega = \xi \cdot \frac{D}{4\pi\eta}\left(-\frac{d\emptyset}{dx}\right) = \xi\,\frac{D}{4\pi \cdot \eta} \cdot E. \qquad [51]$$

This equation is similar to the classic equation [4], but ξ does no more represent Helmholtz's electrokinetic particle potential but a modified electrokinetic potential.

The transport of electric charges in the double layer causes the electrosmotic current (from [44] and [51])

$$J_{\omega} = \frac{e}{l} \cdot u_{\omega} = \xi \cdot \frac{D \cdot a}{2\,\delta} \cdot \xi \frac{D}{4\pi\eta}\left(-\frac{d\text{Ø}}{dx}\right)$$

$$J_{\omega} = \frac{\xi^2 \cdot D^2}{8\,\pi\,\delta} \cdot \frac{a}{\eta}\left(-\frac{d\,\text{Ø}}{d\,x}\right). \qquad [52]$$

On the other hand the electrolytic current J_q within the capillary is

$$J_q = \pi \cdot a^2 \cdot j_q = \pi \cdot a^2 \cdot \frac{1}{\varrho_L} \cdot \left(-\frac{d\,\text{Ø}}{d\,x}\right). \qquad [53]$$

The ratio α_e between the electrosmotic and the electrolytic current is obtained:

$$\alpha_e = \frac{J_{\alpha}}{J_{a}} = \frac{\dfrac{\xi^2 \cdot D^2}{8\pi\delta} \cdot \dfrac{a}{\eta}\left(-\dfrac{d\,\text{Ø}}{d\,x}\right)}{\pi a^2 \cdot \dfrac{1}{\varrho_L}\left(-\dfrac{d\,\text{Ø}}{d\,x}\right)}$$

$$\alpha_e = \frac{2 \cdot \varrho_L}{\eta \cdot \delta} \cdot \left(\frac{\xi \cdot D}{4\,\pi}\right)^2 \cdot \frac{1}{a} = \frac{C}{a} \qquad [54]$$

where C designates the coefficient of double layer effect.

The coefficient α_e indicates the rate of electric current transported by the double layer in proportion to the current transported by electrolysis.

This result of equation [54] has in general already been developed in another way by Smoluchowski and the attempt was made to determine the thickness of double layer from experiments, basing on the Helmholtz theory and this equation $(^{13})$. But the further consequences on the electrosmotic phenomenon were not observed.

Considering equation [54] with respect to the electrosmotic flow the following consideration is now possible:

Since the coefficient α_e characterizes the proportion of current that causes electrosmosis to the electrolytic current, the rate of electrosmotic flow $J\omega$ is:

$$J_{\omega} = \alpha_e \cdot J_a = \frac{C}{a} \cdot J_q\,. \qquad [55]$$

Regarded the limits of electrosmotic flow this means that in contrast to the results of the classic theory for an infinite diameter of capillary the electrosmotic current as well as the discharge now become zero and supposed an extreme capillary diameter of zero, the proportion of electrosmotic current strength to the electrolytic one would be infinite, of course in reality no more realizable. In a definite range of capillary diameter the proportion of electrosmotic to electrolytic discharge of electricity results inversely proportional to the capillary diameter.

The total electric current is obtained:

$$J = J_{\omega} + J_q = J\omega + \frac{J_{\omega}}{\alpha_e} = J\omega\left(\frac{\alpha_e + 1}{\alpha_e}\right)$$

$$J_{\omega} = \frac{\alpha_e}{\alpha_e + 1} \cdot J = \beta_e \cdot J\,. \qquad [56]$$

The coefficient β_e denotes the relation of the electrosmotic current to the total current and therefore will furthermore be called coefficient of electrosmotic action. Expressing it by C and a, β_e results:

$$\beta_e = \frac{\dfrac{C}{a}}{\dfrac{C}{a} + 1} = \frac{1}{1 + \dfrac{a}{C}} \qquad [57]$$

coefficient of electrosmotic action wherein

$$C = \frac{2\varrho_L}{\eta\,\delta}\left(\frac{\xi \cdot D}{4\,\pi}\right)^2.$$

For an infinite radius of the capillary β_e = zero results, that will say, no electrosmotic action would occur. And supposed a = zero the coefficient $\beta_e = 1$ what means that the whole action of electric current would be transformed into electrosmotic current.

With this result one of the forementioned contradictions is put away.

The further question of the relation between the electrokinetic particle potential

ξ respectively ζ and the capillary radius a may now be solved too. For this the coefficient a_e respectively the coefficient of the layer effect C is regarded (eq. [54]):

$$C = \frac{2\,\varrho_L}{\eta\,\delta}\left(\frac{\xi \cdot D}{4\,\pi}\right)^2$$

$$C = 2\,\xi^2 \cdot \frac{\varrho_L}{\eta \cdot \delta}\left(\frac{D}{4\,\pi}\right)^2$$

$$\sqrt{C} = \sqrt{2}\,\xi \cdot \frac{D}{4\,\pi}\sqrt{\frac{\varrho_L}{\eta \cdot \delta}}$$

$$\sqrt{\frac{C}{2\,a}} = \xi \cdot \frac{D}{4\,\pi}\sqrt{\frac{\varrho_L}{a \cdot \eta \cdot \delta}}\,. \qquad [58]$$

Considering eq. [38] it is seen that

$$\frac{D}{4\pi}\sqrt{\frac{\varrho_L}{a \cdot \delta \cdot \eta}} = \frac{1}{\zeta}$$

and, if introduced in eq. [58], there results:

$$\sqrt{\frac{C}{2\,a}} = \frac{\xi}{\zeta} = \varkappa \qquad [59]$$

the ratio of the two electrokinetic particle potentials

$$\xi = \zeta\sqrt{\frac{C}{2\,a}} \qquad [60]$$

$$\zeta = \xi\sqrt{\frac{2\,a}{C}} \qquad [61]$$

and the electrokinetic particle potential ξ results from eq. [38] and [60]:

$$\xi = \sqrt{\frac{C}{2\,a}} \cdot \frac{4\,\pi}{D}\sqrt{\frac{a \cdot \delta \cdot \eta}{\varrho_L}} =$$

$$= \frac{4\,\pi}{D}\sqrt{\frac{C \cdot \delta \cdot \eta}{2\,\varrho_L}}\,. \qquad [62]$$

Since $\dfrac{J_\omega}{J_q} = \dfrac{C}{a}$ (eq. [54]), we may find the relation between ξ and δ, introducing now the specific resistances ϱ_ω of the conducting surface and ϱ_L of the capillary section, where the layers electric resistance R_ω, respectively Ohm's resistance R_q of the interior of capillary mean:

$$R_\omega = \frac{\varrho_\omega \cdot l}{2\,\pi\,a \cdot \delta} \qquad [63]$$

$$R_q = \frac{\varrho_L \cdot l}{\pi \cdot a^2} \qquad [64]$$

and the respective intensities of electric currents:

$$j_\omega = \frac{J_\omega}{2\,\pi\,a \cdot \delta} \qquad [65]$$

$$j_q = \frac{J_q}{\pi \cdot a^2} \qquad [66]$$

We obtain from these expressions, U representing the active potential difference:

$$J_\omega = \frac{U}{R_\omega} = \frac{U}{l} \cdot \frac{2\,\pi\,a \cdot \delta}{\varrho_\omega} =$$

$$J_\omega = \frac{E}{\varrho_\omega} \cdot 2\pi a \cdot \delta \qquad [67]$$

$$j_\omega = \frac{J_\omega}{2\,\pi\,a \cdot \delta} = \frac{E}{\varrho_\omega} \qquad [68]$$

$$J_q = \frac{U}{R_q} = \frac{U}{l} \cdot \frac{\pi \cdot a^2}{\varrho_L} = \frac{E}{\varrho_L} \cdot \pi a^2 \qquad [69]$$

$$j_q = \frac{J_q}{\pi\,a^3} = \frac{E}{\varrho_L} \qquad [70]$$

$$\frac{J_\omega}{J_q} = \frac{\dfrac{E}{\varrho_\omega}}{\dfrac{E}{\varrho_L}} \cdot \frac{2\,\pi a \cdot \delta}{\pi\,a^2} = \frac{\varrho_L}{\varrho_\omega} \cdot \frac{2\,\delta}{a}\,. \qquad [71]$$

Comparing this result with eq. [54], we obtain

$$\frac{C}{a} = \frac{\varrho_L}{\varrho_\omega} \cdot \frac{2\,\delta}{a}$$

$$C = 2 \cdot \frac{\varrho_L}{\varrho_\omega} \cdot \delta\,. \qquad [72]$$

Introducing this result in the ξ-potential of eq. [62], there results

$$\xi = \frac{4\,\pi}{D}\sqrt{\frac{2\,\dfrac{\varrho_L}{\varrho_\omega} \cdot \delta^2 \cdot \eta}{2\,\varrho_L}} =$$

$$= \frac{4\,\pi\delta}{D}\sqrt{\frac{\eta}{\varrho_\omega}}\,. \qquad [73]$$

Comparing now the ξ-potential of eq. [73] with Helmholtz's ζ-potential of eq. [38] we state on the one hand, that taking in consideration the electrolytic process, the electrokinetic particle potential ξ becomes independent of the capillary size and is only a function of physical coefficients. On the opposite the Helmholtz boundary layer potential ζ varies in function of the diameter of capillary.

With this, a further question of stated contradictions is cleared up and we see, that the electrokinetic particle potential ξ represents a physical constant.

From eq. [73] we obtain the thickness δ of the double layer:

$$\delta = \xi \cdot \frac{D}{4\pi} \sqrt{\frac{\varrho_\omega}{\eta}} \cdot \qquad [74]$$

If the specific electric resistance of double layer is the same as the specific resistance of the liquid phase itself we obtain:

$$\delta = \xi \cdot \frac{D}{4\pi} \cdot \sqrt{\frac{\varrho_L}{\eta}} \qquad [75]$$

By introducing this result in eq. [54] we obtain the electric current J_q of the capillary section:

$$\frac{J_\omega}{J_q} = \frac{2\varrho_L}{\eta} \cdot \frac{1}{\xi} \cdot \frac{4\pi}{D} \sqrt{\frac{\eta}{\varrho_L}} \cdot \frac{\xi^2 \cdot D^2}{16\pi^2} \cdot \frac{1}{a}$$

$$\frac{J_\omega}{J_q} = \frac{1}{2} \sqrt{\frac{\varrho_L}{\eta}} \cdot \frac{\xi \cdot D}{\pi} \cdot \frac{1}{a} = \alpha_e = \frac{C}{a} \qquad [76]$$

$$C = \frac{1}{2} \sqrt{\frac{\varrho_L}{\eta}} \cdot \frac{\xi \cdot D}{\pi}$$

(coefficient of double layer effect)

$$J_q = J_\omega \cdot \frac{2\pi}{\xi \cdot D} \sqrt{\frac{\eta}{\varrho_L}} \cdot a \,. \qquad [77]$$

The total current flowing through the capillary results:

$$J = J_\omega + J_q - J_\omega + J_\omega \cdot \frac{2\pi}{\xi \cdot D} \sqrt{\frac{\eta}{\varrho_L}} \cdot a$$

$$\mathrm{J} = J_\omega \left(1 + \frac{2\pi}{\xi \cdot D} \sqrt{\frac{\eta}{\varrho_L}} \cdot a\right) \qquad [78]$$

and the double layer current becomes:

$$J_\omega = \frac{J}{1 + \frac{2\pi}{\xi \cdot D} \sqrt{\frac{\eta}{\varrho_L}} \cdot a} = \beta_e \cdot J \qquad [79]$$

$$\beta_e = \frac{1}{1 + \frac{2\pi}{\xi \cdot D} \sqrt{\frac{\eta}{\varrho_L}} \cdot a}$$

β_e being the coefficient of electrosmotic action.

Until now no hypothesis on the composition of the flow of liquid has been made. Basing on the preceeding considerations, with regard to the electric phenomenon we have to do with two electric currents of different action, on the one hand the electrolytic current J_q transporting the ions in both directions, on the other hand an electrosmotic current J_ω within the double layer transporting the electric charges of the boundary layer. Both currents influence the flow of electric charges and with this the flow of the liquid contained in the capillary.

With respect to the flow of liquid the classic theory supposes, that the interior part of liquid moves with the boundary layers speed u_ω (Fig. 4) respectively u_c, an assumption that leads to the forementioned contradictions incompatible to experience. Since the layers speed u_ω (eq. [51]) is independent from the capillary size the electrosmotic discharge would increase in proportion to a^2, if the classic assumption really would be valid.

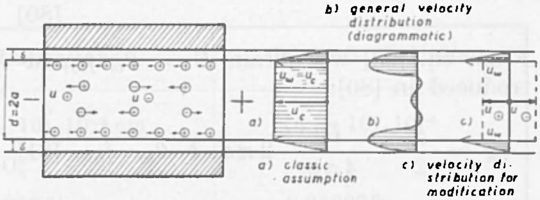

Fig. 4. – Electro-osmotic-electrolytic flow and velocities.

But other distributions of capillary speeds are conceivable. By the former developments only the layers speed u_ω respectively u_c has been determined. Considering the motion of ions at the interior, these ones are moving in both directions and the general velocities diagram representing the resultant of differential motions will have a certain form, that in reality is not yet known (Fig. 4b).

Let us consider another assumption and its consequences. The opposite extreme with regard to classic assumption would be, that the boundary layer flows independently from the interior with a speed u_ω, the resultant of velocity of ions within the capillary section being zero, the velocities of positive and negative ions compensating mutually. The flow would represent some sort of film motion of the boundary layer. With these assumptions we obtain from eq. [51].

$$u_\omega = \xi \cdot \frac{D}{4\pi\eta} \cdot \mathrm{E} \cdot \qquad [51]$$

Assuming, that within the boundary layer of thickness δ u increases linearly from zero to u_ω (Fig. 4c) the discharge Q of liquid phase becomes:

$$Q = \frac{u_\omega}{2} \cdot 2\,\pi a \cdot \delta = u_\omega \cdot \pi \cdot a \cdot \delta$$

$$Q = \frac{\xi}{2} \cdot \frac{D}{4\pi\eta} \cdot 2\pi a \cdot \delta \cdot E = \xi \cdot \frac{D}{4\eta} \cdot a \cdot \delta \cdot E \qquad [80]$$

From eq. [68] we obtain $E = \varrho_\omega \cdot j_\omega$, introduced in [80]:

$$Q = \frac{\xi}{2} \cdot \frac{D}{4\pi\eta} \cdot 2\,\pi a \cdot \delta \cdot \varrho_\omega \cdot j_\omega \cdot \qquad [81]$$

Since $2\pi a . \delta . j_\omega = J_\omega$ (eq. [68]) the result is:

$$Q = \xi \cdot \frac{\varrho_\omega \cdot D}{8\,\pi\eta} \cdot J_\omega \cdot \qquad [82]$$

The deductions hitherto made, supposed a difference between the specific electric resistance ϱ_ω and ϱ_L, since it is not sure that the electric properties of liquid within the interior of the capillary and the boundary layer are identical. For the following consideration we put $\varrho_\omega = \varrho_L$ and start from eq. [82]:

Introducing from eq. [56] $J_\omega = \beta_e . J$ there results:

$$Q = \xi \cdot \frac{\varrho_L \cdot D}{8\,\pi\eta} \cdot \beta_e \cdot J \cdot \qquad [83]$$

Eq. [79] introduced in eq. [82] furnishes:

$$Q = \xi \cdot \frac{\varrho_L \cdot D}{8\,\pi\eta} \cdot \frac{J}{1 + \dfrac{2\,\pi}{\xi \cdot D}\sqrt{\dfrac{\eta}{\varrho_L}} \cdot a}$$

$$Q = \xi^2 \cdot \frac{\varrho_L \cdot D}{8\,\pi\eta} \cdot \frac{J}{\xi + \dfrac{2\,\pi}{D}\sqrt{\dfrac{\eta}{\varrho_L}} \cdot a}$$

$\dfrac{\varrho_L \cdot D}{8\pi\eta} = A, \dfrac{2\,\pi}{D}\sqrt{\dfrac{\eta}{\varrho_L}} \cdot a = B$ (abbreviations)

$$Q = \xi^2 \cdot A \cdot \frac{J}{\xi + B}$$

$$\frac{Q}{J} = \xi^2 \cdot A \cdot \frac{1}{\xi + B}$$

$$\frac{Q}{J}(\xi + B) = \xi^2 \cdot A$$

$$\xi^2 \cdot A - \xi \cdot \frac{Q}{J} - B \cdot \frac{Q}{J} = 0$$

$$\xi^2 - \xi \cdot \frac{1}{A} \cdot \frac{Q}{J} - \frac{B}{A} \cdot \frac{Q}{J} = 0$$

$$\xi = \frac{Q}{J} \cdot \frac{1}{2\,A} \pm \sqrt{\left(\frac{Q}{J} \cdot \frac{1}{2A}\right)^2 + \frac{Q}{J} \cdot \frac{B}{A}}$$

$$= \frac{Q}{J} \cdot \frac{1}{2A} \pm \sqrt{\left(\frac{Q}{J} \cdot \frac{1}{2A}\right)^2 + \frac{4Q^2}{4J^2} \cdot \frac{AB}{A^4} \cdot \frac{J}{Q}}$$

$$\xi = \frac{Q}{J} \cdot \frac{1}{2A} \pm \sqrt{\left(\frac{Q}{J} \cdot \frac{1}{2A}\right)^2 \cdot \left(1 + 4AB \cdot \frac{J}{Q}\right)}$$

$$= \frac{Q}{J} \cdot \frac{1}{2A} \pm \frac{Q}{J} \cdot \frac{1}{2A}\sqrt{1 + 4AB \cdot \frac{J}{Q}}$$

$$\xi = \left(\frac{Q}{J} \cdot \frac{1}{2A}\right)\left(1 \pm \sqrt{1 + 4AB \cdot \frac{J}{Q}}\right) \qquad [84]$$

$$\frac{1}{2\,A} = \frac{4\,\pi\eta}{\varrho_L \cdot D}$$

$$4AB = 4 \cdot \frac{\varrho_L \cdot D}{8\pi\eta} \cdot \frac{2\pi}{D} \sqrt{\frac{\eta}{\varrho_L}} \cdot a = $$

$$= \sqrt{\frac{\varrho_L}{\eta}} \cdot a$$

$$\xi = \frac{Q}{J} \cdot \frac{4\pi\eta}{\varrho_L \cdot D} \left(1 \pm \sqrt{1 + \frac{J}{Q} \sqrt{\frac{\varrho_L}{\eta}} \cdot a}\right)$$

$$a = \frac{d}{2} \; (d = \text{diameter of capillary})$$

$$\xi = \frac{Q}{J} \cdot \frac{4\pi\eta}{\varrho_L \cdot D} \left(1 \pm \sqrt{1 + \frac{J}{2Q} \sqrt{\frac{\varrho_L}{\eta}} \cdot d}\right) \qquad [85]$$

This expression allows to check the electrokinetic particle potential ξ from experiments. Together with eq. [75] the thickness of double layer may be determined.

The former investigators having evaluated numerous experiments basing on the Helmholtz formula, the relation between the ζ– and ξ–potentials is very useful for comparison of results.

Basing on eq. [4] the discharge in Helmholt'z expression is deduced:

$$Q = \pi a^2 \cdot u_c = \zeta \cdot \frac{\varrho_L \cdot D}{4\pi\eta} \pi a^2 \cdot j_c \qquad [86]$$

$$\pi a^2 \cdot j_c = J$$

$$Q = \zeta \frac{\varrho_L \cdot D}{4\pi\eta} \cdot J. \qquad [87]$$

The electrokinetic particle potential ζ (Helmholtz) is obtained:

$$\zeta = \frac{Q}{J} \cdot \frac{4\pi\varrho}{\varrho_L \cdot D} \cdot \qquad [88]$$

The ratio $\varkappa$ (eq. [59]) of the two electrokinetic particle potentials may now be determined (eq. [85] and [88]):

$$\varkappa = \frac{\xi}{\zeta} =$$

$$= \frac{\frac{Q}{J} \cdot \frac{4\pi\eta}{\varrho_L \cdot D} \left(1 + \sqrt{1 + \frac{J}{2Q} \sqrt{\frac{\varrho_L}{\eta}} \cdot d}\right)}{\frac{Q}{J} \cdot \frac{4\pi\eta}{\varrho_L \cdot D}}$$

$$\varkappa = 1 + \sqrt{1 + \frac{J}{2Q} \sqrt{\frac{\varrho_L}{\eta}} \cdot d} . \qquad [89]$$

For obtaining now an idea of the order of magnitude of the electrokinetic particle potential ξ as defined a formerly executed experiment of K. Illig and N. Schönfeldt with a glass-Filter (Schott & Gen., Jena) and $CuSO_4$–solution, containing complete indications for determining $\varkappa$, is used (14,15). The magnitudes of this experiment were:

Magnitudes		Indications	In C. G. S.-Units
Diameter of pores	d	$(5 \div 10) \cdot 10^{-4}$ cm	$(5 \div 10) . 10^{-4}$
Solution		$CuSO_4$	
Concentration . .	c	0,05693 %	0,05693 %
Conductibility . .	λ	$3{,}32 \cdot 10^{-4}\, \Omega^{-1}\, cm^{-1}$	—
Specific electric resistance . . .	ϱ_L	$3{,}01 \cdot 10^3\, \Omega\, cm$	$3{,}35 \cdot 10^{-9}$
Dielectric constant	D	78	78
Viscosity.	η	0,0123 Poises	0,0123
Discharge	Q	$9{,}26 \cdot 10^{-4}\, cm^3/sec$	$9{,}26 . 10^{-4}$
Current strength .	J	$5 . 10^{-3}$ Amp	$15 . 10^6$
Electrokinetic particle potential (Helmholtz)	ζ	— 0.01153 Volt	—

The transforming coefficient $\varkappa$ according to eq. [89] results:

$$\varkappa = 1 +$$

$$+\sqrt{1+\frac{15\cdot 10^{6}}{2\cdot 9{,}26\cdot 10^{-4}}\sqrt{\frac{3{,}35\cdot 10^{-9}}{1{,}23\cdot 10^{-2}}}(5\div 10)\cdot 10^{-1}}$$

$$\varkappa = 46{,}8 \div 65{,}8$$

and the electrokinetic particle potential as defined is:

$$\underline{\xi} = \varkappa\,.\,\zeta = -0{,}01153\,(46{,}8 + 65{,}8) =$$

$$= -\underline{(0{,}54 \div 0{,}76)}\ \text{Volt.}$$

From this calculation follows, that the ξ-potential shows an order of magnitude of 10^{-1} — 10^{0} Volts.

Comparing this result with the galvanic potentials we see on the one hand from table 3 that the electrokinetic particle potentials according to Helmholtz exhibit the order of magnitude of about 10^{-2} Volts. On the other hand the absolute normal potentials own the order of magnitude of 10^{-1} — 10^{0} Volts (table 1).

Basing on the assumptions made in the preceeding considerations the modified ξ-potential shows too the order of Volts. Hence the outlined hypothesis as well as the other reflexions combined lead to the conclusion, that the electrokinetic particle potential probably is a simple contact potential apparent to the potential of galvanic chains and of the same order of magnitude.

ABSTRACT

Summarizing, the detailed study of the electrosmotic phenomenon leads to the following results:

From the consideration of the electrosmotic flow as a partial electric surface current always combined with electric current caused by the interfering electrolytic processus follows that the contradictions resulting from application of the classic theory, when applied to special problems, e.g. the electrosmotic rise in function of capillary diameter, disappear. With the increase of capillary diameter, the electrosmotic effect decreases in accordance to experience, while from the classic theory the opposite effect results.

Taking in consideration the electrolytic part of current the modified electrokinetic particle potential results constant, a real physical magnitude and independent from the capillary diameter as must be expected basing on the original definition of the particle potential.

Supposing the electrosmotic part of flow to be some sort of film motion the modified electrokinetic potentials show an order of magnitude of Volts and seem to represent simple contact potentials similar to galvanic potential differences and with these results the precariousnesses of the classic theory seem to vanish.

The theoretic deductions of the present paper treating the nature of electrosmotic phenomenon represent a hypothesis, that aims at avoiding the contradictions arising from application of the known theory, when applied beyond it's limits. The theory outlined cannot solve definitively the question of the nature of the electrokinetic particle potential, since it bases only on physical reflexions. For a complete knowledge of this magnitude direct measurements of electrosmotic particle potentials not yet available would have to be esecuted i. e. the determination of potential differences between non-conductors and aqueous solutions. But the theoretic considerations made give the allusion, that the electrokinetic particle potentials seem to be apparented to the contact potentials known of the galvanic chains. This indication is supported by the fact that the definitions of contact potentials and electrokinetic particle potentials in fond are identical. But the experiments show, that on the one hand the absolute potential of silver e.g. is 1.077 Volt (table 1). On the opposite it's electrokinetic particle potential deduced from the Helmholtz formula varies from 0.032-0.048 Volts (table 3) Since from the two potentials a difference of order of magnitude results, there arises the question of the causes of this considerable difference and the real nature of the electrokinetic particle potential.

RIASSUNTO

La Memoria inizia con una breve esposizione delle ipotesi e dei risultati delle teorie classiche sull'effetto elettrosmotico nei tubi

capillari, sviluppate da Helmholtz, Lamb e Perrin.

La teoria di Helmholtz assume che in uno strato liquido di spessore piccolissimo δ adiacente alla parte del capillare (strato limite), si stabilisca una (d.d.p.) differenza di potenziale (potenziale elettrocinetico, e.c.) fra il liquido e la parete: inoltre, tale teoria suppone che il moto del liquido sia laminare, con velocità variabile linearmente da zero sulla parete, fino ad un massimo (u_c) conseguito a distanza dalla parete stessa: tale velocità massima si mantiene costante nella massa del liquido fuori dello strato limite.

Helmholtz giunge ad una relazione che mostra come la velocità (u_c) risulti proporzionale al campo impresso, al potenziale e.c. alla costante dielettrica e sia indipendente dallo spessore δ dello strato limite.

Lamb considera lo strato limite come un doppio strato elettrico di spessore δ, in cui la parte non adiacente alla parete del capillare si sposta sotto l'azione del campo elettrico esterno, contrariamente ad Helmholtz, il moto del liquido non è supposto laminare. La formula che si deduce da questa ipotesi differisce da quella di Helmholtz per un termine moltiplicativo, che diviene uguale all'unità quando si faccia l'ulteriore ipotesi del moto laminare.

Perrin, facendo sostanzialmente le stesse ipotesi di Helmholtz, giunge alle stesse relazioni. La differenza sta nel modo di trattazione, estremamente semplificato mediante la considerazione dello strato limite come un condensatore. Inoltre Perrin pone in relazione il potenziale e.c. con il potenziale normale del solido rispetto alla soluzione e con l'attività ionica, il che costituisce un primo tentativo di spiegazione teorica dell'esistenza del potenziale e.c., fino al lavoro di Perrin semplicemente constatata.

Con l'ausilio delle teorie classiche ora esposte, è facile mettere in relazione la velocità di filtrazione v_e (proporzionale al campo applicato) con la velocità u_c di efflusso del liquido da uno dei capillari costituenti il filtro. Secondo l'A. e sulla base delle ipotesi classiche il coefficiente di filtrazione (rapporto fra la velocità di filtrazione e il campo) sarebbe proporzionale al potenziale elettrocinetico. La conoscenza del coefficiente di filtrazione (facilmente misurabile sperimentalmente) permette, di conseguenza, di calcolare il potenziale e.c.: il calcolo, condotto da vari studiosi, su diverse sostanze, conduce a valori del potenziale e.c. dell'ordine di 10^{-2} volt.

Le teorie classiche dell'effetto elettrosmotico non vanno esenti da obiezioni, e talvolta prevedono fatti che l'esperienza non conferma. Per esempio, secondo tutte le formule dedotte dalle teoria citate, la portata del flusso elettrosmotico varia in ragion diretta del quadrato del raggio del capillare, mentre l'esperienza mostra che l'efflusso raggiunge un massimo per un certo raggio del capillare, oltre il quale non è più possibile osservare alcun effetto apprezzabile; di più alcuni materiali a grana fina (quali per esempio, la bentonite) mostrano efflussi uguali, o anche maggiori, di materiali più grossolani, come fanghi o polveri di quarzo.

Le prime teorie classiche portano ad espressioni del potenziale e.c. che dipendono dal raggio del capillare: questo fatto è difficilmente spiegabile dal punto di vista fisico. Inoltre si assegna al potenziale e.c. un ordine di grandezza di 10^{-2} volt.; mentre i potenziali di contatto delle catene galvaniche (che, secondo l'A., rappresenterebbero le conseguenze di fenomeni analoghi all'effetto elettroosmotico) sono dell'ordine del volt.

Infine, le teorie classiche trascurano completamente i fenomeni elettrolitici, ovviamente sempre presenti nella massa del liquido, e che contribuiscono in maniera non trascurabile al trasporto di corrente.

Per superare tutte queste difficoltà, l'A. espone una sua teoria sull'effetto elettrosmotico combinato con quello elettrolitico.

Le ipotesi sono sempre le stesse, il potenziale e.c. è definito ancora come d.d.p. fra strato limite e fase solida, il flusso elettrosmotico è considerato laminare: in più, nel flusso di corrente interviene in modo essenziale l'effetto elettrolitico. Con queste premesse, l'A. deduce, per l'effetto elettrosmotico, una espressione formalmente identica a quella di Helmholtz e Perrin, determina il rapporto fra corrente elettrosmotica e corrente elettrolitica, che risulta inversamente proporzionale al raggio del capillare: il che porta di conseguenza che, per raggi grandissimi, la corrente è tutta elettrolitica, per raggi piccolissimi tutta elettrosmotica.

Inoltre, l'A. giunge ad una espressione del *potenziale e.c. indipendente dal raggio del capillare, e di ordine di grandezza molto più grande di quello previsto dalle teorie classiche; l'ordine di grandezza è ricondotto a quello delle catene galvaniche.*

Per quanto riguarda il calcolo della portata, l'A. fa l'ipotesi che il trasporto dovuto all'effetto elettrolitico sia complessivamente nullo e che il trasporto effettivo avvenga solo per effetto elettrosmotico, ed abbia quindi sede solo sullo strato limite: come conseguenza si ha una formula per il potenziale e.c., che permette di calcolare lo spessore dello strato limite.

In conclusione, la teoria esposta dall'A. tende ad eliminare alcune delle più gravi contraddizioni fra teorie classiche ed esperienza dell'effetto elettrosmotico, e completare quest'ultime, fornendo per esempio, il modo di calcolare lo spessore dello strato limite. Per contro, non entra in merito al meccanismo di formazione del potenziale e.c., se non con l'ipotesi che sia del tipo «potenziale di contatto» di catene galvaniche: anzi l'A. stesso raccomanda uno studio più approfondito di tale parte del fenomeno, chiave di volta dell'intero effetto.

REFERENCES

(1) Casagrande, L., *Review of Past and Current Work on Electro-Osmotic Stabilization of Soils.* Report to the Bureau of Yards and Docks, Harvard Soil Mechanics Series, **45**, Harvard University, Cambridge, Mass. (1953).

(2) Schaad, W. und Haefeli, R., *Die Anwendung der Elektrizität zur Entwässerung und Verbesserung feinkörniger Bodenarten,* Bulletin der Vereinigung Schweizerischer Petrolgeologen und Ingenieure, **42**, Mai (1946) and Strasse und Verkehr, **23/24**, (1946).

(3) — — *Elektrokinetische Erscheinungen und ihre Anwendung in der Bodenmechanik,* Schweiz. Bauzeitung, **65**, Nr. 16-18, Zurich (1947).

(4) — — *Zastosowanie elektrycznoszi do odwaniania i melioracji gruntów drnobnoziarnistych,* Obdudowa, 3, (1946).

(5) — — *Electro-Kinetic Phenomena and their Application to Soil Mechanics,* National Research Council of Canada. Division of Building Research, **61**, Ottawa (1948).

(6) Casagrande, L., *Electro-Osmosis in Soils,* Géotechnique, **1**, Nr. 3, June (1949).

(7) Winterkorn, H. F., *Fundamental Similarities between Electro-Osmotic and Thermo-Osmotic Phenomena,* Proc. Highay Res. Board. **27**, pp. 443-455, (1947).

(8) Helmholtz, H., *Studien über elektrische Grenzschichten,* Wiedemanns Annalen der Physik und Chemie, **7**, Leipzig (1879).

(9) Lamb, H., *On the Theory of Electric Endosmosis and other allied Phenomena, and on the Existence of a Sliding Coefficient for a Fluid in Contact with a Solid,* Philosophical Magazine, 25, London (1888)

(10) Perrin, J., *Mécanisme de l'électrisation de contact et solutions colloidales,* Journ. Chim. Phys. **2**, (1904).

(11) Kuhn, W., *Physikalische Chemie,* Wepf & Cie, Basel (1947).

(12) Schaad, W., *Electrical Treatment of Soils,* Proc. Int. Conf. Soil Mech. and Found. Engg. Rotterdam (1948), **VI**, p. 85.

(13) v. Smoluchowski, M., *Elektrische Endosmose und Strömungsströme,* Graetz's Handbuch der Elektrizität und des Magnetismus, Leipzig (1912).

(14) Illig, K., und Schoenfeldt, N., *Untersuchungen an Diaphragmen Wissenschaftliche Veröffentlichungen Siemens-Konzern,* **VI**, Springer Berlin (1927).

(15) Prausnitz, P. H., und Reitstötter, J., *Elektrophorese, Elektroosmose, Elektrodialyse,* Th. Steinkoppf, Dresden u. Leipzig (1931).

(16) Belluigi, A., *Vollständige Entwässerung des Wasseresättiften Bodens durch Elektrosmose, die Baubechnitz* (Berlin), Januar 1957.

(17) — *Teoria generale dell'elettrogeosmosi tridimensionale,* Geofisica pura e applicata, **47**, pp. 90-102 (1957).

(18) — *Fenomeni elettrocinetici provocati in terreni cilindrici (fori di sonda, con fanghi etc.) saturi d'acqua (applicazioni varie).* Metano petrolio e nuove energie, N. 8, 1957.