V. ELECTROKINETIC PHENOMENA

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§ 1. HISTORICAL INTRODUCTION; DESCRIPTION OF ELECTRO-KINETIC PHENOMENA

a. Generalities

In the foregoing chapters electrokinetic phenomena have been mentioned several times (Chapter II, Chapter IV). These phenomena have been investigated extensively by electro-chemists and colloid chemists because they can yield valuable information on the electrochemical double layer [1].

Although HELMHOLTZ [2] had already indicated in principle, how the connection between electrokinetic phenomena and the structure of the double layer has to be interpreted, later investigations have shown that a quantitative interpretation meets with several obstacles. Even at the present moment one cannot say that a completely satisfactory situation has been reached. Nevertheless so many important data on the electrochemical double layer have been derived from electrokinetic phenomena, that we feel completely justified in devoting a separate chapter to them.

By electrokinetic phenomena we mean phenomena involving electricity and connected with a tangential movement of two phases along each other. They may arise either from an external electric field directed along the phase boundary and resulting in a movement, or from a movement of the phases along each other, resulting in a transport of electricity. Examples of the first kind are electro-osmosis and electrophoresis, of the second kind, streaming-potential and migration potential.

b. Electro-osmosis

Electro-osmosis (also called electro-endosmosis) is the movement of a liquid with respect to a solid wall as the result of an applied potential gradient. It can be observed in an arrangement shown diagrammatically in Fig. 1.

P represents a porous plug (which may be replaced also by a single capillary tube). When a potential difference is set up between the electrodes E_1 and E_2, the liquid is driven through the plug [3]. This flow of liquid can be measured by the displacement of

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[1] A very good survey on the subject has been given by H. A. ABRAMSON, *Electrokinetic phenomena and their application to biology and medicine*, New York 1934 (To be cited as ABRAMSON book).

[2] H. HELMHOLTZ, *Wied. Ann.*, 7 (1879) 337.

[3] Electro-osmosis must be distinguished from water transport by electrolysis, which depends only on the constitution of the liquid and is independent of the material of the plug. It may complicate measurements of electro-osmosis in concentrated solutions, *cf.* H. C. HEPBURN, *Proc. Phys. Soc. London*, 39 (1927) 99; 43 (1931) 524; 45 (1933) 755.

the meniscus M in the capillary tube. The direction and the velocity of the liquid stream depend upon the properties of the plug and of the solution. In order to avoid gas being developed at the electrodes, it will often be necessary to use reversible electrodes such as Ag-AgCl or, for larger currents, Zn-saturated solution of $ZnSO_4$. LANGE and CRANE [1] describe a set up capable of determining the electro-osmosis also in nonaqueous solutions with electrodes of the $Zn-ZnSO_4$ type.

The use of a single capillary instead of the plug P gives the advantages of a much easier cleaning of the apparatus, a better reproducibility of the results and an easier
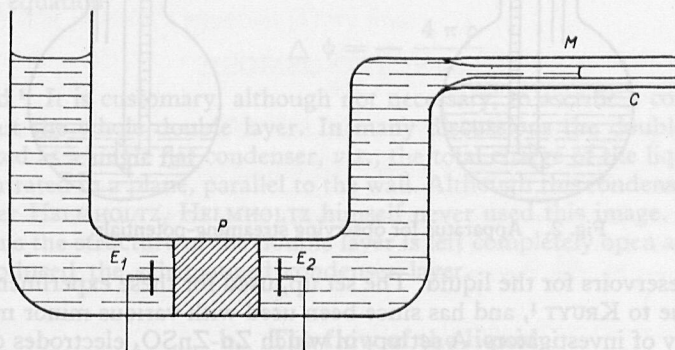

Fig. 1. Apparatus for observing electro-osmosis.

interpretation. On the other hand the quantity of liquid displaced through a single capillary is much smaller, and therefore more difficult to measure than the displacement through a plug which acts as a great number of capillaries. Moreover, there are only a few materials, (quartz, glass) from which capillaries can be made, whereas the construction of a porous plug is always possible.

Electro-osmosis was discovered by REUSS [2] in 1808 and has been investigated extensively by WIEDEMANN [3] and QUINCKE [4].

The theoretical interpretation has been given by HELMHOLTZ [5], LAMB [6], PERRIN [7] and especially by VON SMOLUCHOWSKI [8].

c. Streaming potential

The apparatus used for measuring electro-osmosis can also be used for observing streaming potentials. When the liquid is forced through the porous plug by an external pressure, a potential difference (the streaming-potential) can be measured between the

[1] E. LANGE and P. W. CRANE, Z. physik. Chem., A 141 (1929) 225.
[2] F. F. REUSS, Mémoires de la Société Impériale des Naturalistes de Moscou, 2 (1809) 327.
[3] G. WIEDEMANN, Pogg. Ann., 87 (1852) 321; 99 (1856) 177.
[4] G. QUINCKE, Pogg. Ann., 113 (1861) 513.
[5] H. HELMHOLTZ, Wied. Ann., 7 (1879) 337.
[6] H. LAMB, Phil. Mag., (5) 25 (1888) 52.
[7] J. PERRIN, J. chim. phys., 2 (1904) 601.
[8] M. VON SMOLUCHOWSKI, cf. particularly his contribution in GRAETZ, Handbuch der Elektrizität und des Magnetismus II, Leipzig 1914, p. 366, where all older literature is reviewed and already many of the essential considerations of this chapter are given in a beautiful and refined mathematical form

electrodes E_1 and E_2. In this case much larger quantities of liquid are displaced, and the resulting potential difference is much smaller than in the case of electro-osmosis. It is therefore desirable to modify the apparatus in order to meet the special requirements by using reversible electrodes for E_1 and E_2 (*e.g.*, chlorinated silver electrodes) and by
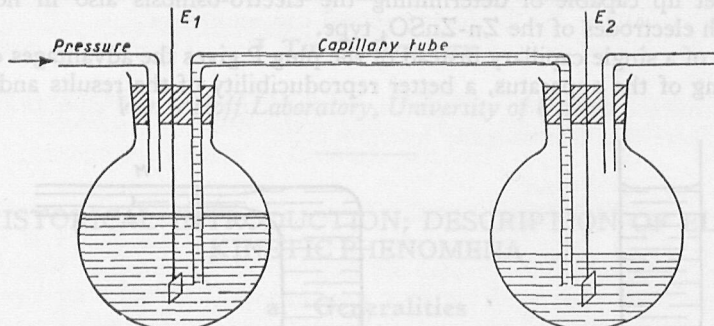
Fig. 2.   Apparatus for observing streaming-potentials.

adding large reservoirs for the liquid. The set up, used for these experiments as shown by Fig. 2 is due to KRUYT [1], and has since been used with various minor modifications by the majority of investigators. A set up, in which Zn-$ZnSO_4$ electrodes can be used, has been given by FREUNDLICH and RONA [2].

d.   Electrophoresis

By electrophoresis (or cataphoresis as it was called formerly) we mean the movement of colloidal particles in an electric field. It is in every respect comparable to the mobility of electrolytic ions and can be measured in much the same ways as those by which ionic mobilities are determined. In the methods of electrophoresis we shall recognise the determinations of the transport number, the moving boundary as well as the analytical method. Moreover, the ultramicroscopic visibility of colloidal particles offers the means of studying their electrophoretic mobility directly under the ultramicroscope. These methods are discussed in greater detail in § 7 of this chapter.

e.   Migration potential

The reverse effect of electrophoresis arises when small particles which are suspended in a liquid are forced to move, say by gravitation or by an ultrasonic or a centrifugal field. Then an electric field is generated in the direction of the movement and a potential difference can be measured between two electrodes in the liquid, one at the top, the other at the bottom of the vessel. This potential difference is called migration potential or potential of falling particles and the effect is indicated as the DORN-effect [3]. The experiments are difficult and as yet only few results have been obtained [4].

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[1] H. R. KRUYT, *Kolloid-Z.*, 22 (1918) 81.

[2] H. FREUNDLICH and P. RONA, *Sitz. ber. preuss. Akad. Wiss. Physik. math. Klasse*, 20 (1920) 397.

[3] E. DORN, *Wied. Ann.*, 10 (1880) 46, *cf.* also J. STOCK, *Bull. intern. Acad. sci. Cracovie*, A (1913) 131; (1914) 95.

[4] E. F. BURTON and J. C. CURRIE, *Phil. Mag.*, (6) 49 (1925) 194; A. J. RUTGERS, *Nature*, 157 (1946) 74.

§ 2.   STARTING-POINT FOR THE ANALYSIS OF ELECTROKINETIC PHENOMENA. THE ZETA-POTENTIAL

a.   Introduction

All electrokinetic phenomena have to be explained by the interaction between a flow of electricity and a flow of liquid in the double layer.

For the mathematical analysis of these phenomena, the precise structure of the double layer may often be left out of consideration, the only essential feature being, that POISSON's equation

$$\triangle \psi = - \frac{4 \pi \rho}{\varepsilon} \tag{1}$$

is satisfied [1]. It is customary, although not necessary, to ascribe a constant value to ε throughout the whole double layer. In many discussions the double layer has been schematized as a single flat condenser, *viz.*, the total charge of the liquid is thought to be concentrated in a plane, parallel to the wall. Although this condenser layer is usually called after HELMHOLTZ, HELMHOLTZ himself never used this image. In HELMHOLTZ's calculations the structure of the double layer is left completely open and it was PERRIN who introduced the schematized condenser layer.

b.   The flow of the liquid

As to the flow of the liquid, one postulates a purely laminar flow, with a coefficient of viscosity, η, having the same value throughout the whole system. There have been some differences of opinion concerning the boundary conditions of the movement of the liquid. In considerations using PERRIN's condenser layer, the liquid is assumed to be at rest in a plane coinciding with the charge on the wall. HELMHOLTZ and especially LAMB [2] have taken account of the possibility of a slip along the wall, but no experimental evidence in favour of such a slip has ever been found.

In considerations based upon the image of a diffuse double layer it has been assumed, for reasons to be explained more precisely in § 3a. 2, that the movement of the liquid does not begin immediately next to the wall, but that a layer of the liquid with a thickness of one molecule or a few molecules, is stationary with respect to the wall.

c.   The zeta-potential

It appears that, in all modes of calculation, the electrical potential in the slipping-plane between the fixed and the flowing liquid is determinative for the electrokinetic phenomena. This potential is usually called the *zeta-potential* (ζ).

d.   Structure of the double layer

Our considerations on electrokinetics will be based upon the image of the double layer, as developed by STERN [3] and we shall consider the possibilities of a slipping-plane

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[1] The introduction of the dielectric constant ε, omitted by HELMHOLTZ is due to PELLAT, *cf.* J. PERRIN, *J. chim. phys.*, 2 (1904) 607.

[2] H. LAMB, *Phil. Mag.*, (5) 25 (1888) 52.

[3] *Cf.* Chapter IV, § 4d, p. 132.

situated in the STERN-layer, in the diffuse layer, or just in the transition plane between the two. We too shall consider η and ε as constants (eventually accounting for a different but constant ε in the STERN-layer). As long as concrete data concerning this point are lacking, the introduction of a variable η or ε would indeed result in a more general formulation, but the arbitrariness arising therefrom would make any test delusive.

Entering upon further details of the structure of the double layer proves to be unnecessary. It is only in the case of electrophoresis that it may become necessary to account for the specific charges and mobilities of the ions out of which the double layer is formed. We return to this point in section 6.

§ 3.   ON ELECTRO-OSMOSIS

a.   Electro-osmotic velocity

a. 1.   *Slipping plane in the diffuse layer*

We consider the electro-osmotic movement along a flat surface under the influence of an electric field E directed parallel to the surface. The potential-distribution in the double-layer is given by the theory of STERN (*cf.* Chapter IV) and is schematically represented in Fig. 3.
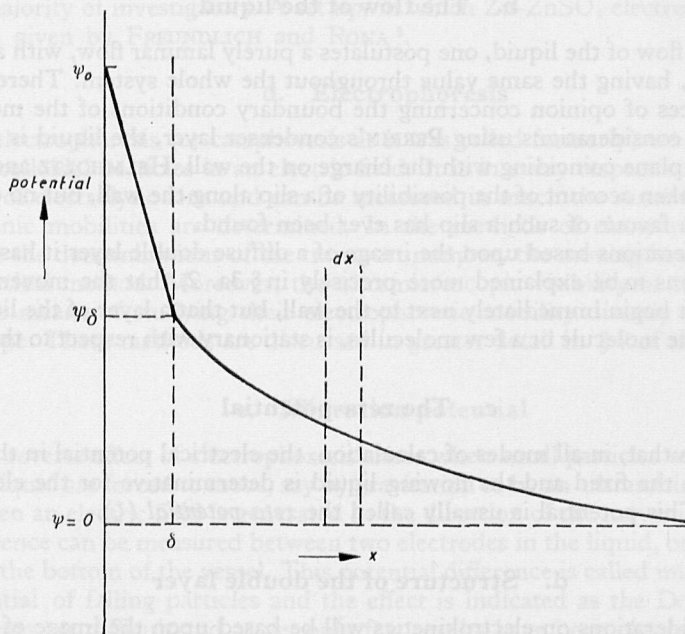

Fig. 3.   Potential distribution in the double layer.

When the field E is applied, a stationary state is reached after a short starting period. In this stationary state each layer, dx, of the liquid moves with a uniform velocity parallel to the wall, because the total force on such a layer is zero. We have

to distinguish two sorts of forces, *viz.*, the force exerted by the external field E on the ions in the layer and transferred by the liquid friction to the layer as a whole[1], and the frictional forces exerted on the considered layer by the neighbouring layers moving with a different velocity.

Consequently in the stationary state

$$E \cdot \rho \cdot dx = \eta \left(\frac{dv}{dx} \right)_x + dx \frac{d}{dx} \eta \left(\frac{dv}{dx} \right)_x = \eta \cdot \frac{d^2 v}{dx^2} dx \tag{2}$$

Inserting POISSON's equation (1) we find

$$-\frac{E \varepsilon}{4 \pi} \frac{d^2 \psi}{dx^2} = \eta \frac{d^2 v}{dx^2} \tag{3}$$

Now equation (3) has to be integrated over the whole liquid as far as it can move, that is between $x = \infty$ and the slipping-plane. Assuming for the present that the slipping-plane is situated in the diffuse layer and recalling that

$$\text{for } x = \infty \qquad \psi_\infty = \left(\frac{d\psi}{dx} \right)_\infty = 0, \left(\frac{dv}{dx} \right)_\infty = 0,$$

for the slipping-plane $\psi = \zeta$, $v = 0$

and calling the velocity of the liquid at a large distance from the wall v_E, the electro-osmotic velocity, we find

$$v_E = \frac{\varepsilon \zeta E}{4 \pi \eta} \tag{4}$$

This classical expression for the electro-osmosis is often derived on the basis of a condenser double-layer[2]. But it follows from the derivation given above, that the same expression is found on the basis of the diffuse double-layer, contrary to the opinion expressed by FREUNDLICH[3].

a. 2.   *Slipping-plane in the* STERN-*layer*

Assuming now, that the slipping-plane is situated somewhere in the STERN-layer, we may describe the movement in the GOUY-layer by the theory given in § 3a. 1, resulting for this case in

$$v_E - v_\delta = \frac{\varepsilon \psi_\delta E}{4 \pi \eta} \tag{5}$$

The stationary state of the layer of adsorbed ions, situated at $x = \delta$ is given by

$$E \sigma_1 = \eta \left(\frac{dv}{dx} \right)_{\text{GOUY}} - \eta' \left(\frac{dv}{dx} \right)_{\text{STERN}} \tag{6}$$

where σ_1 is the charge of the adsorbed layer per cm².

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[1] That the force acting primarily on the ions, may be considered to act on the liquid layer as a whole, is made clear by the following argument. In the stationary state the ions have uniform velocity; so the total force on the ions must be zero. This total force is composed of the force exerted by the field and the frictional force exerted by the liquid. In virtue of NEWTON's law (action = reaction) a force of the same magnitude is exerted by the ions upon the liquid and consequently the force on the liquid has the same value as the force acting directly on the ions in the liquid.

[2] For instance J. PERRIN, *J. chim. phys.*, 2 (1904) 601.

[3] H. FREUNDLICH, *Kapillarchemie I*, Leipzig 1930, p. 359.

From the theory of electricity it follows that

$$\sigma_1 = \frac{\varepsilon'}{4\,\pi}\left(\frac{\mathrm{d}\,\psi}{\mathrm{d}x}\right)_{\text{STERN}} - \frac{\varepsilon}{4\,\pi}\left(\frac{\mathrm{d}\,\psi}{\mathrm{d}x}\right)_{\text{GOUY}}$$

if ε' is the dielectric constant in the STERN-layer.

Combining this expression with (6) and recalling that

$$\frac{E\,\varepsilon}{4\,\pi}\left(\frac{\mathrm{d}\,\psi}{\mathrm{d}x}\right)_{\text{GOUY}} = -\,\eta\left(\frac{\mathrm{d}v}{\mathrm{d}x}\right)_{\text{GOUY}}$$

We find

$$\frac{E\,\varepsilon'}{4\,\pi}\left(\frac{\mathrm{d}\,\psi}{\mathrm{d}x}\right)_{\text{STERN}} = -\,\eta'\left(\frac{\mathrm{d}v}{\mathrm{d}x}\right)_{\text{STERN}} \tag{7}$$

Calling the potential of the slipping-plane again ζ, integration of (7) leads to

$$v_\delta = \frac{\varepsilon'\,(\zeta - \psi\delta)\,E}{4\,\pi\,\eta'}$$

With the aid of (5) we find finally

$$v_E = \frac{E}{4\,\pi}\left[\frac{\varepsilon'\,(\zeta - \psi\delta)}{\eta'} + \frac{\varepsilon\,\psi\delta}{\eta}\right] \tag{8}$$

or more generally

$$v_E = \frac{E}{4\,\pi}\int_0^\zeta \frac{\varepsilon}{\eta}\,\mathrm{d}\psi \tag{8a}$$

Usually ε and η are considered as constants. In that case the normal proportionality between v_E and ζ is found. Some authors assume a constant value of η but doubt the constancy of ε and interpret the electrokinetic phenomena not in terms of ζ but of the moment of the double layer ($\int \varepsilon\,\mathrm{d}\zeta$). GUGGENHEIM [1] proposed to call the electrokinetic unit of $\frac{\varepsilon\,\zeta}{4\,\pi}$ the "HELMHOLTZ".

When we nevertheless retain the old method of calculation notwithstanding certain difficulties in the estimation of dielectric constant and viscosity, this is done because after all ζ is the important quantity for our knowledge of the double layer. It has to be compared with the total potential of the double layer and with the potential of the diffuse layer, and in this way valuable information may be obtained concerning the internal structure of the double-layer. It was just the very early observation [2], that there was an evident disparity between the total potential (NERNST potential) as determined by the potential-determining ions and the ζ-potential calculated from electrokinetics which lead to the introduction of a slipping-plane situated somewhere in the liquid and not exactly at the phase boundary.

[1] E. A. GUGGENHEIM, *Trans. Faraday Soc.*, 36 (1940) 139.
[2] H. FREUNDLICH and P. RONA, *l.c.*, page 196; H. FREUNDLICH and G. ETTISCH, *Z. physik. Chem.*, 116 (1925) 401.

b. Volume of liquid transported by electro-osmosis

Although a direct measurement of the electro-osmotic velocity (v_E) is possible [1], it is more usual to determine the volume of liquid displaced through a capillary or porous plug by electro-osmosis. If we consider a capillary with a constant cross-section O, the volume displaced per sec. is given by

$$\text{vol} = O \cdot v_E = \frac{O \zeta \varepsilon E}{4 \pi \eta} \tag{9}$$

In this expression it is supposed that the whole mass of liquid inside the capillary is displaced with a velocity v_E. This is only exactly true for the bulk of the liquid in the capillary, outside the reach of the double layer. The rate of displacement of the liquid in the double layer is smaller than v_E. Consequently (9) may only be applied when the diameter of the capillary is large in comparison with the thickness of the double layer. As the thickness of the double layer is generally smaller than 10^{-5} cm and the diameter of the capillary is mostly larger than 10^{-3} cm the condition is amply fulfilled.

It is possible to eliminate O from eq. (9) by applying Oнм's law

$$O \cdot E = \frac{1}{\lambda} \cdot i \tag{10}$$

where i represents the current through the capillary and λ the specific conductivity of the liquid.

By combination of (9) and (10) the displaced volume is now expressed in the easily measurable quantities i and λ

$$\text{vol} = \frac{\varepsilon \zeta i}{4 \pi \eta \lambda} \tag{11}$$

Nevertheless there is a certain danger in the application of (10) and therefore of (11) caused by the so-called surface conductance. As a consequence of the accumulation of ions in the double layer there exists an excess conductance along the surface of the capillary. This excess conductance may be of the same order of magnitude as the conductance through the bulk of the liquid, especially in dilute solutions, and the proportionality between i and λ is lost. In that case (10) should be replaced by

$$O E \lambda + S E \lambda_s = i \tag{12}$$

where λ_s is the specific surface conductance and S the circumference of the capillary. Then (11) becomes

$$\text{vol} = \frac{\varepsilon \zeta i}{4 \pi \eta \left(\lambda + \dfrac{S \lambda_s}{O} \right)} \tag{13}$$

It is possible to determine the necessary corrections by measuring the resistance of the

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[1] *cf.* The ultramicroscopic technique for the determination of the electrophoretic velocity mentioned in § 7 e, p. 218.

capillary when filled with dilute and concentrated solutions of an electrolyte [1] or by applying eq. (9), where the conductance through the capillary plays no part.

c.   Electro-osmosis through a plug of arbitrary geometry

It is the merit of VON SMOLUCHOWSKI [2] to have shown that equation (11) retains its validity, if in the experiment of electro-osmosis the capillary is replaced by a porous plug. His demonstration proceeds along the following lines.

In a porous plug, in which *the diameter of the pores is much larger than the thickness of the double layer*, the lines of force of the applied electrical field in the double layer run practically parallel to the walls of the pores. They cause an electro-osmotic movement of the liquid along the wall. Just outside the double layer the velocity of the liquid (u) is directed parallel to the wall and its value is given by

$$u = \frac{\varepsilon \zeta E}{4 \pi \eta} \qquad (14)$$

where E is the local field strength, which is also parallel to the wall because the material of the plug is considered to be an insulator.

Now we have to consider how the liquid flows through the plug if the velocity of the liquid is given by (14) everywhere at the boundary between plug material and liquid. The liquid is practically incompressible and the electricity too flows as if it were an incompressible liquid. As the flows of electricity and of the liquid at the boundary are parallel and proportional to each other the most simple and obvious solution of the problem is the supposition that (14) holds not only at the boundary but throughout the whole liquid phase.

The above may be expressed by a more rigorous formalism. The electric field is determined by the condition

$$\text{div } E = 0 \text{ and curl } E = 0$$

with the boundary condition that the component of E perpendicular to the wall is zero.
The liquid stream obeys the equation (for slow laminar motion)

$$\text{div } u = 0 \text{ and } \eta \text{ curl curl } u = - \text{ grad } p$$

The value of v at the wall is given by (14) and the pressure (p) is equal on both sides of the plug.
Then (14) is satisfied through the whole liquid in the plug. As curl $E = 0$, curl $u = 0$ too and consequently $p = $ constant. If p is different on the two sides of the plug an ordinary flow of liquid under external pressure is superimposed on the electro-osmotic flow (14) *cf.* § 3d.

To convert eq. (14), valid for any point of the liquid into the integral expression (11), we have to integrate (14) over the whole cross-section of the diaphragm.
The total electrical current i is given by

$$i = \int E \, \lambda \, d\omega \qquad (15)$$

where the integral has to be taken over a complete, though arbitrary cross-section.

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[1] ABRAMSON book, page 97; J. J. BIKERMAN, *Kolloid-Z.*, 72 (1935) 100; H. L. WHITE, B. MONAGHAN, and F. URBAN, *J. Phys. Chem.*, 40 (1936) 207; P. W. O. WIJGA, *Thesis*, Utrecht 1946.
[2] M. VON SMOLUCHOWSKI, *Bull. intern. acad. sci. Cracovie*, 1903, p. 184.

The total amount of the liquid passing per second is

$$\text{vol} = \int u \, d\omega$$

which by applying (14) and (15) can be transformed into

$$\int u \, d\omega = \int \frac{\varepsilon \zeta E}{4 \pi \eta} \, d\omega = \frac{\varepsilon \zeta}{4 \pi \eta} \int E \, d\omega = \frac{\varepsilon \zeta}{4 \pi \eta} \frac{i}{\lambda}$$

Herewith the validity of (11) for an arbitrary plug is demonstrated. For the case however, where the plug has a considerable surface conductance not only does eq. (11) no longer describe the electro-osmosis, but it is impossible to apply a correction for it, as was done for a single capillary. Experiments by WIJGA [1] and theoretical work by OVERBEEK and WIJGA [2] and by VAN EST [3] lead to the conclusion that safe results with plugs can only be obtained if the surface conductance is negligible.

d. Electro-osmotic counter pressure

Another method of determination of the electro-osmosis consists in the measurement of the counter pressure generated by the electro-osmotic displacement of the liquid. This counter pressure causes the liquid to flow back through the capillary or plug. In the stationary state the electro-osmotic flow is just counterbalanced by the backflow.

The pressure-head P, which may be measured in an apparatus such as Fig. 1 with an oblique or vertical capillary C, is for the case of electro-osmosis through a single capillary determined by POISEUILLE's law

$$\text{vol} = \frac{\pi P r^4}{8 \eta l} = \frac{\pi r^2 \varepsilon \zeta E}{4 \pi \eta}$$

or
$$P = \frac{2 \varepsilon E l \zeta}{\pi r^2} = \frac{2 \varepsilon i l \zeta}{\pi^2 \lambda r^4} \tag{16}$$

The method can also be applied to the electro-osmosis through a plug [4] (without surface conductance).

We postpone the extensive discussion of the results of electro-osmotic experiments until after the treatment of the other electrokinetic phenomena, because we are less interested in the electrokinetic phenomena themselves than in the ζ-potential as a common feature of them all.

At this point we mention only that the linear dependence on the field-strength E, the current i, the proportionality of P with E/r^2 (eq. (16)) and the independence of the displaced volume of the dimensions of the diaphragm have been repeatedly tested and confirmed [5].

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[1] P. W. O. WIJGA, *Thesis*, Utrecht 1946.

[2] J. TH. G. OVERBEEK and P. W. O. WIJGA, *Rec. trav. chim.*, 65 (1946) 556.

[3] W. T. VAN EST, *unpublished work*.

[4] See ABRAMSON book, page 59.

[5] G. WIEDEMANN, *Pogg. Ann.*, 87 (1852) 321; 99 (1856) 177; G. QUINCKE, *Pogg. Ann.*, 113 (1861) 513; M. DE SMET, *Mededeel. Koninkl. Vlaam. Acad. Wetenschap. Belg. Klasse Wetenschap.*, 3 (1941) no. 12, p. 14.

§ 4.   STREAMING POTENTIALS

A calculation of the streaming potential can be based upon the following considerations (see Fig. 2). The difference of pressure applied to the ends of the capillary (or to both sides of the porous plug) causes a flow of liquid through the capillary. This liquid stream carries along with it the charge of the double layer and so is the bearer of an electric convection current. As a consequence of this transport of charge a potential difference arises between the ends of the capillary, which causes a conduction current through the capillary directed oppositely to the convection current. In the stationary state, the convection current, which is proportional to the pressure difference P, just counterbalances the conduction current, which is proportional to the potential difference E. Consequently the streaming potential E is proportional to the pressure P. The factor of proportionality can be determined by a reasoning given below in small print, and is equal to

$$\frac{E}{P} = \frac{\varepsilon\,\zeta}{4\,\pi\,\eta\,\lambda} \tag{17}$$

independent of the dimensions of the plug or capillary [1]. Conditions which are to be satisfied for the validity of eq. (17) are:

a.   The flow of the liquid must be laminar, a condition which is easily fulfilled in practice.
b.   The radius of curvature of the capillary or of the pores of the plug must be much larger than the thickness of the double layer.
c.   The conductance determining the conduction current should depend solely on the bulk conductivity of the liquid. The surface conductance should not play a part of any importance. If this condition is not fulfilled, as is very often the case, corrections can sometimes be applied to which we shall return later on.

A derivation of eq. (17) will now be given for a plug of arbitrary geometry.

The convection current i_1, through an arbitrary (not necessarily plane) cross section of the plug or capillary is given by

$$i_1 = \int v_n\,\rho\,\mathrm{d}f \tag{18}$$

where v_n is the component of the velocity of the liquid normal to $\mathrm{d}f$, ρ the charge density, and $\mathrm{d}f$ an infinitesimal part of the cross section. With the aid of POISSON's theorem (18) may be transformed into

$$i_1 = -\frac{\varepsilon}{4\pi}\int v_n\,\varDelta\,\psi\,\mathrm{d}f \tag{19}$$

If the extension of the double layer is small compared with the curvature of the circumference of the cross section f, $\varDelta\,\psi$ may be put equal to $\mathrm{d}^2\psi/\mathrm{d}N^2$ where N is the normal to the wall of the pores and $\mathrm{d}f$ can be replaced [2] by $\mathrm{d}S\mathrm{d}N$ where $\mathrm{d}S$ is an element of the circumference (see Fig. 4). This approximation is permissible because only that part of f is important where $\varDelta\,\psi$ is significantly
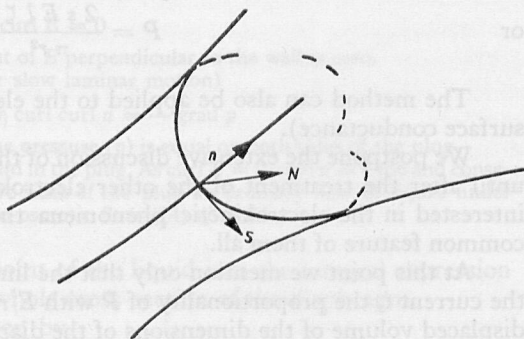

Fig. 4.   Cross-section through part of the plug.

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[1] Just as in the case of electro-osmosis the product $\dfrac{\varepsilon\,\zeta}{\eta}$ valid for a slipping-plane in the Gouy-ayer, may be replaced by $\displaystyle\int_0^\zeta \frac{\varepsilon}{\eta}\,\mathrm{d}\psi$ for a more general case.

[2] At its circumference the cross section f is supposed to be perpendicular to the wall.

different from zero. Eq. (19) may then be transformed in the following way by partial integrations

$$i_1 = -\frac{\varepsilon}{4\pi}\int v_n \; \Delta\psi \; \mathrm{d}f = -\frac{\varepsilon}{4\pi}\iint v_n \frac{\mathrm{d}^2\psi}{\mathrm{d}N^2}\mathrm{d}N\mathrm{d}S = \frac{\varepsilon}{4\pi}\iint \frac{\mathrm{d}v_n}{\mathrm{d}N}\cdot\frac{\mathrm{d}\psi}{\mathrm{d}N}\mathrm{d}N\mathrm{d}S =$$

$$= -\frac{\varepsilon}{4\pi}\int \zeta \frac{\mathrm{d}v_n}{\mathrm{d}N}\mathrm{d}S - \frac{\varepsilon}{4\pi}\iint \psi \frac{\mathrm{d}^2 v_n}{\mathrm{d}N^2}\mathrm{d}N\mathrm{d}S \tag{20}$$

The product $\dfrac{\delta v_n}{\delta N}\,\mathrm{d}S$ may be replaced by $\mathrm{curl}\,\mathbf{v}\cdot\mathrm{d}S$ because the n and N components of curl $\mathbf{v}$ do not contribute to the product and $\dfrac{\delta v_N}{\delta n}$ is zero.

So the expression for i_1 becomes

$$i_1 = -\frac{\varepsilon\zeta}{4\pi}\int \mathrm{curl}\,\mathbf{v}\,\mathrm{d}S - \frac{\varepsilon}{4\pi}\iint \psi \frac{\delta^2 v_n}{\delta N^2}\mathrm{d}N\mathrm{d}S$$

which with the aid of STOKES' theorem transforms into

$$i_1 = -\frac{\varepsilon\zeta}{4\pi}\int \mathrm{curl}_n\;\mathrm{curl}\,\mathbf{v}\,\mathrm{d}f - \frac{\varepsilon}{4\pi}\iint \psi \frac{\delta^2 v_n}{\delta N^2}\mathrm{d}N\mathrm{d}S$$

The second term may now be neglected because $\dfrac{\delta^2 v_n}{\delta N^2}$ and curl_n curl $\mathbf{v}$ are of the same order of magnitude but ψ is only comparable to ζ in a very thin layer near to the wall.

Now the hydrodynamic equation for laminar movement

$$\eta\;\mathrm{curl}\;\mathrm{curl}\,\mathbf{v} = -\;\mathrm{grad}\,p$$

(p is the hydrostatic pressure) can be applied and i_1 is found to be

$$i_1 = \frac{\varepsilon\zeta}{4\pi\,\eta}\int \mathrm{grad}_n\,p\,\mathrm{d}f \tag{21}$$

The conduction current i_2 is equal to

$$i_2 = -\int \lambda\,\mathrm{grad}_n\,V\,\mathrm{d}f \tag{22}$$

where V is the potential caused by the streaming of the liquid.

In the stationary state i_1 has to be equal to $-i_2$ and thus

$$\frac{\displaystyle\int \mathrm{grad}_n\,V\,\mathrm{d}f}{\displaystyle\int \mathrm{grad}_n\,p\,\mathrm{d}f} = \frac{\varepsilon\zeta}{4\pi\,\eta\,\lambda}$$

If in every cross section the quotient $\dfrac{\mathrm{grad}_n\,V}{\mathrm{grad}_n\,p}$ is equal to $\varepsilon\,\zeta/4\,\pi\,\eta\,\lambda$ the ratio E/p between two

points on the two sides of the porous plug has the same value, so that the validity of equation (17) is demonstrated for a general case, provided the conditions a-c mentioned above are applicable.

The constancy of the quotient E/p has been repeatedly confirmed [1] provided the pressure was not so high as to cause turbulent flow.

[1] cf. H. B. BULL, Kolloid-Z., 66 (1934) 20; H. R. KRUYT and P. C. VAN DER WILLIGEN, Kolloid-Z., 45 (1928) 307.

In many researches on streaming potential a relatively low value of E/p was found when the solution contained little or no electrolyte. Formerly this has been ascribed to a low value of the ζ-potential. By later investigations it has become clear that for these very dilute solutions the condition b mentioned on page 204 is no longer fulfilled. The bulk conductivity λ is so small that the surface conductance begins to play a rôle and the return current i_2 is larger than the normal value given by equation (22). This results in a depression of the value of E.

It is not difficult to make the necessary corrections for the surface conductance, if the streaming potential is determined for a capillary of radius r. In that case the return current is proportional to (λ_s is the specific surface conductance)

$$\pi\, r^2\,\lambda + 2\,\pi\,r\,\lambda_s$$

instead of to $\pi r^2 \lambda$ and the corrected equation for the streaming potential becomes

$$E/p = \frac{\varepsilon\,\zeta}{4\,\pi\,\eta\left(\lambda + \dfrac{2\,\lambda_s}{r}\right)} \tag{23}$$

The correction can be applied either by a direct evaluation of the resistance of the capillary [1] or by a comparison of the streaming potentials in capillaries of different diameters[2]. If the streaming potential is determined in a porous plug, an analogous correction has been applied by various authors [3], but just as in the case of electro-osmosis this correction is too simple and leads usually to values of the ζ-potential which are smaller than the real ones.

§ 5. RELATION BETWEEN ELECTRO-OSMOSIS AND STREAMING POTENTIAL

Comparing the relations (11) for electro-osmosis and (17) for streaming potential one observes that both phenomena can be described by the same constant

$$\frac{\text{vol}}{i} = \frac{E}{P} = \frac{\varepsilon\,\zeta}{4\,\pi\,\eta\,\lambda} \tag{24}$$

Even when the correction for surface conductance is applied to a single capillary (eq. 13 and 23) relation (24) is found to remain valid.

It has been shown by MAZUR and OVERBEEK [4] that the validity of this relation is of a very general character and a direct consequence of ONSAGER's [5] principle of reciprocity of irreversible phenomena.

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[1] H. L. WHITE, B. MONAGHAN, and F. URBAN, *J. Phys. Chem.*, 40 (1936) 207; P. W. O. WIJGA, *Thesis*, Utrecht 1946. A. J. RUTGERS and M. DE SMET, *Trans. Faraday Soc.*, 43 (1947) 102.

[2] A. J. RUTGERS, *Trans Faraday Soc.*, 36 (1940) 69.

[3] D. R. BRIGGS, *J. Phys. Chem.*, 32 (1928) 641; W. M. MARTIN and R. A. GORTNER, *ibid.*, 34 (1930); H. B. BULL and R. A. GORTNER, *ibid.*, 35 (1931) 307.

[4] P. MAZUR and J. TH. G. OVERBEEK, *Rec. trav. chim.* 70 (1951) 83; *cf.* also J. TH. G. OVERBEEK and P. W. O. WIJGA, *Rec. trav. chim.*, 65 (1946) 556.

[5] L. ONSAGER, *Phys. Rev.*, 37 (1931) 405; 38 (1931) 2265; H. B. G. CASIMIR, *Revs. Modern Phys.*, 17 (1945) 343.

The relation (24) as such has been known for a long time and it was already tested in 1892 by SAXÉN[1].

This means that as far as the properties of the double layer are involved an experiment on streaming potential gives exactly the same information as one on electro-osmosis. From these experiments it is only possible to derive a value for the ζ-potential, if either surface conductance is negligible or if the experiment is carried out on a single capillary. See this chapter § 3c p. 203.

§ 6.　ON ELECTROPHORESIS

a.　Theoretical treatment neglecting relaxation

The phenomenon of electrophoresis may be considered from two standpoints which seem to differ fundamentally, but which on nearer consideration prove to lead to exactly the same result for the velocity of electrophoresis.

First one may consider electrophoresis to be caused by the force exerted on the *charge* of the moving particle by the applied external field. In that case it can be described by STOKES' formula (in the case of a spherical particle of radius a)

$$v = \frac{e\,E}{6\,\pi\,\eta\,a} \tag{25}$$

where e is the charge of the particle. This expression, however, needs to be corrected for the influence of the ionic atmosphere (double layer) in exactly the same way as is done for the mobility of ions in the theory of DEBYE and HÜCKEL.

The other way of attacking the problem starts immediately with the electric double layer and considers electrophoresis as the converse of electro-osmosis. Indeed, in electro-osmosis we deal with a moving liquid and a fixed solid surface, whereas in electrophoresis the liquid as a whole is at rest and the solid particle is in movement. In both cases the relative movement of the liquid phase with respect to the solid surface is controlled by the forces applied to the double layer. In this way the velocity of electrophoresis can be derived directly from the equation (4) for electro-osmosis and is given by : [2]

$$v_E = \frac{\varepsilon\,\zeta\,E}{4\,\pi\,\eta} \tag{26}$$

In this expression the particle is considered to be exposed to a homogeneous electric field of strength E. The shape of the particle is of no importance just as the electro-osmosis equation (11) is valid for an arbitrary shape of the porous plug. Restrictions on the applicability of expression (26) are similar to the case of electro-osmosis:

α. the double-layer must be thin compared with the dimensions of the particle,

β. the particle must be insulating and the surface conductance at the interface must be so small that the distribution of the external field is practically uninfluenced by it.

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[1] U. SAXÉN, *Wied. Ann.*, 47 (1892) 46.

[2] If desired the expression $\varepsilon\zeta/\eta$ can be replaced by $\int \frac{\varepsilon}{\eta}\,\mathrm{d}\psi$ as in equation (8a) for electro-osmosis.

This condition is equivalent to

$$\lambda_{surf} \ll \lambda a \qquad (27)$$

if a is one of the main dimensions of the particle.

For a long time eq. (26) was held to describe the electrophoresis velocity in practically all cases irrespective of the restrictions given above. But in 1924 HÜCKEL [1], basing himself upon the knowledge newly gained in the theory of the conductance of strong electrolytes, gave another expression for the electrophoretic velocity, differing from (26) by a factor 2/3

$$v_E = \frac{\varepsilon \, \zeta \, E}{6 \, \pi \, \eta} \qquad (28)$$

This expression was derived by correcting STOKES' equation (25) for the so-called electrophoretic retardation caused by the action of the external field on the double layer. Under the influence of the external field the counter ions are driven in a direction opposite to that of the particle. They impart their movement to the liquid surrounding them and in this way cause a flow of liquid in the wrong direction. Thus it is as if the particle does not move in a stationary liquid but in a moving liquid; the electrophoretic velocity is decreased. The exact calculation of this effect results in eq. (28).

At first sight there seems to be a discrepancy at least in the numerical value of the two electrophoresis equations pointing to a non-equivalence of the two methods of calculation.

HENRY [2], however, established that the discrepancy is not of a fundamental nature, but is a consequence of the fact, that in VON SMOLUCHOWSKI's calculation the deformation of the electrical field by the presence of the insulating particle is implicitly taken into account whereas in HÜCKEL's method the field in the double layer and in the bulk of the liquid is not influenced by the presence of the particle. This last treatment is only allowed, either if the conductivity of the particle is exactly equal to that of the liquid, or if the dimensions of the particle are so small compared with the thickness of the double layer that in the greater part of the double layer the deformation of the field is not appreciable.

By an accurate mathematical treatment, resembling HÜCKEL's method, but now taking account fully of the deformation of the external field by the presence of the colloidal particle, HENRY was able to show that the electrophoretic velocity is in all cases equal to $f \varepsilon \zeta E / \pi \eta$, the numerical factor f depending upon the value of $\varkappa a$, where a is the radius of the spherical or cylindrical particle (HENRY considered only these two shapes of the particle) and $\varkappa$ represents the reciprocal thickness [3] of the double layer, $\varkappa$ being equal to

$$\varkappa = \sqrt{\frac{8 \, \pi \, e^2 \, \Sigma \, n z^2}{\varepsilon \, kT}}$$

The value of f is equal to $\frac{1}{4}$ for a cylindrical particle with its axis in the direction of the field, varies between 1/4 and 1/8 for a cylinder perpendicular to the field and varies between 1/4 and 1/6 for a spherical particle, as illustrated in Fig. 5.

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[1] E. HÜCKEL, *Physik. Z.*, 25 (1924) 204.
[2] D. C. HENRY, *Proc. Roy. Soc. London*, 133 (1931) 106.
[3] *cf.* Chapter IV, § 4c, eq. 40 p. 128.

Thus the calculations of HENRY are in complete accord with the equation of VON SMOLUCHOWSKI, demanding that $f = \frac{1}{4}$ irrespective of the shape of the particle, when $\varkappa a$ is large and also in accord with HÜCKEL's equation for a sphere ($f = 1/6$ for $\varkappa a$ is small).

HENRY also considered the influence of a certain conductivity of the particles which alters the distribution of the electric field in the neighbourhood of the particles completely. As can be expected this has no influence on the electrophoresis in the case of a very thick double layer ($\varkappa a \ll 1$) but when the double layer is thin, the electro-

$$f = \frac{\pi \eta}{\varepsilon \zeta E} v_E$$
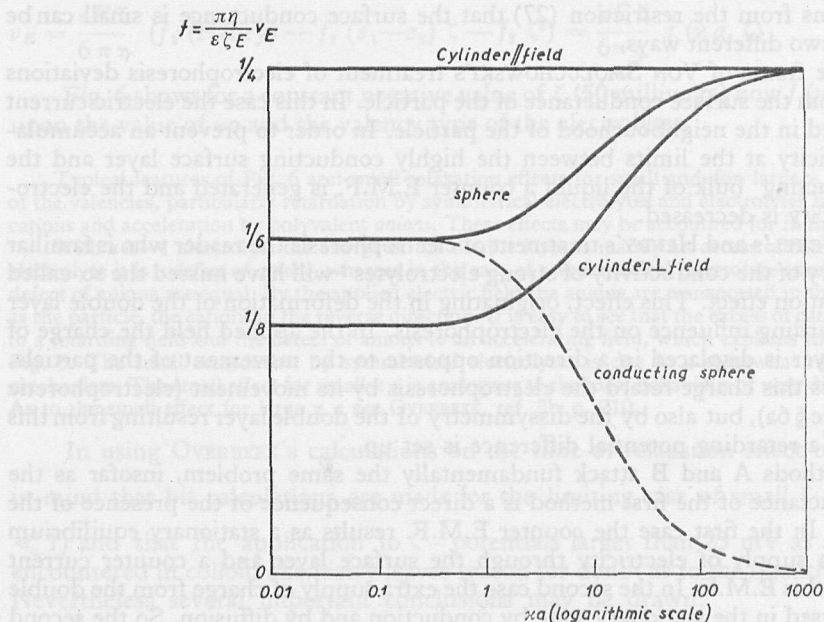
Fig. 5. Dependence of the electrophorectic velocity on the ratio between the radius (a) of the particle and the thickness ($1/\varkappa$) of the double layer.

phoretic velocity is diminished and in extreme cases even nullified (*cf.* Fig. 5 where the factor of proportionality f for a conductive sphere is given). HENRY and BRITTAIN [1] demonstrated such an extreme case by showing that the electrophoretic movement of a silver wire in a moderately concentrated solution of silver nitrate (conducting cylinder $\perp$ field, $\varkappa a \gg 1$) is not perceptible.

In most practical cases of metallic colloidal particles, however, it is almost certain that the influence of the conductance of the particles is neutralized by the polarization at the surface, a polarization tension of a few microvolts [2] being sufficient to stop any further passage of electricity through the particle. In this case the particle behaves as if it consisted of a non-conducting substance.

[1] D. C. HENRY and J. BRITTAIN, *Proc. Roy. Soc. London*, A 143 (1931) 130.
[2] Usually electrophoresis is carried out at a field strength of the other of 10 volts/cm. The diameter of colloidal particles is of the order of 10^{-6} cm, the tension over the particle being thus 10 μV.

b. The influence of relaxation

It is necessary now to consider the different restrictions used in the derivation of the electrophoresis equations and answer the question if these restrictions are necessary and justified and if it is possible to indicate how the necessary corrections can be applied. In the last part of the previous subsection, it has already been indicated how the electrophoretic velocity is influenced when the restriction that the double layer is thin is no longer satisfied.

Deviations from the restriction (27) that the surface conductance is small can be envisaged in two different ways.

A. In the frame of VON SMOLUCHOWSKI's treatment of electrophoresis deviations may result from the surface conductance of the particle. In this case the electric current is concentrated in the neighbourhood of the particle. In order to prevent an accumulation of electricity at the limits between the highly conducting surface layer and the weakly conducting bulk of the liquid a counter E.M.F. is generated and the electrophoretic velocity is decreased.

· B. In HÜCKEL's and HENRY's treatment of electrophoresis the reader who is familiar with the theory of the conductivity of strong electrolytes [1] will have missed the so-called time-of-relaxation effect. This effect, originating in the deformation of the double layer also has a retarding influence on the electrophoresis. In the applied field the charge of the double layer is displaced in a direction opposite to the movement of the particle. Not only does this charge retard the electrophoresis by its movement (electrophoretic retardation see § 6a), but also by the dissymmetry of the double layer resulting from this displacement a retarding potential difference is set up.

Both methods A and B attack fundamentally the same problem, insofar as the surface conductance of the first method is a direct consequence of the presence of the double layer. In the first case the counter E.M.F. results as a stationary equilibrium between extra supply of electricity through the surface layer and a counter current originated by this E.M.F. In the second case the extra supply of charge from the double layer is dispersed in the stationary state by conduction and by diffusion. So the second method is perhaps able to describe the time-of-relaxation effect in more detail, but fundamentally there is no difference between the two methods.

The problem of the influence of the time-of-relaxation effect on electrophoresis has been attacked by various authors [2]. They treat it in different ways and different approximations. Owing to the mathematical intricacies their results are far from satisfying. More recently OVERBEEK [3], BOOTH [4] and HENRY [5] independently have given new treatments of this effect. BOOTH [4a] and OVERBEEK [3a] treated the relaxation effect for spherical insulating particles surrounded by a GOUY double layer. BOOTH [4b] and

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[1] see *e. g.* D. A. MACINNES, *The principles of electrochemistry*, New York 1939, p. 326 or any other modern textbook on electrochemistry.

[2] H. H. PAINE, *Trans. Faraday Soc.*, 24 (1928) 412; M. MOONEY, *J. Phys. Chem.*, 35 (1931) 331; J. J. BIKERMAN, *Z. physik. Chem.*, A 171 (1934) 209; S. KOMAGATA, *Researches Elektrotech. Lab. Tokyo*, No. 387 (1935). J. J. HERMANS, *Phil. Mag.*, (7) 26 (1938) 650.

[3]a. J. TH. G. OVERBEEK, *Thesis*, Utrecht 1941; *Kolloid Beihefte*, 54 (1943) 287; b. J. TH. G. OVERBEEK, *Philips Research Repts.* 1 (1946) 315; c. See also: J. TH. G. OVERBEEK in *Advances in Colloid Science* III, New York 1950, 97—135.

[4]a F. BOOTH, *Nature*, 161 (1948) 83, *Proc. Roy. Soc. London*, A 203 (1950) 514.

[4]b F. BOOTH, *Trans. Faraday Soc.*, 44 (1948) 955.

[5] D. C. HENRY, *Trans. Faraday Soc.*, 44 (1948) 1021.

HENRY [1] both considered the influence of a large surface conductance and found that it could depress the electrophoretic velocity considerably, especially for small particles.

As at the moment of writing this chapter details of the treatment of BOOTH [2] were not yet available, we shall now give a short description of OVERBEEK's results. In the provisional paper by BOOTH it is mentioned that the results of these two authors are in fair agreement. OVERBEEK found that the counter E.M.F. of relaxation is in the first approximation proportional to ζ for unsymmetrical electrolytes and to ζ^2 for symmetrical electrolytes. The resulting electrophoresis equation is of the form

$$v_E = \frac{\varepsilon E \zeta}{6 \pi \eta} \; (f_1 \, (\text{Henry}) - f_2 \, (z_1 - z_2) \, \zeta - f_3 \, \zeta^2) = \frac{\varepsilon E \zeta}{6 \pi \eta} \; f \, (\varkappa \, a, \zeta) \tag{29}$$

Fig. 6 shows for a constant negative value of ζ (50 millivolts) how $f \, (\varkappa a, \zeta)$ depends upon the value of $\varkappa a$ and the valency type of the electrolytes.

Typical features of Fig. 6 are: small relaxation effects for small and for large $\varkappa \, a$, the spreading of the valencies, particularly retardation by symmetrical electrolytes and electrolytes having polyvalent cations and acceleration by polyvalent *anions*. These effects may be accounted for in the following way.

With a 4—1 electrolyte the charge of the double layer is mainly an excess of cations, with a 1—4 electrolyte it is *a defect of anions*, whereas in the case of a symmetrical electrolyte excess of cations and defect of anions are equal. By the applied electric field the anions are transported in the same direction as the particle, the cations in the reverse direction. It is easy to see that the excess of cations so gives rise to a retarding field and the defect of anions to an accelerating field, which explains the valency rule of Fig. 6. The small retardation by symmetrical electrolytes is due to a somewhat more complicated mechanism. The small effect for small $\varkappa \, a$ is analogous to the ideal behaviour of very dilute electrolytes. As to the small effect for large $\varkappa \, a$ see OVERBEEK, ref. 3b p. 210.

In using OVERBEEK's calculations on the time-of-relaxation effect one must keep in mind that his calculations are made for the limiting case of small ζ-potentials ($\frac{\varepsilon \, \zeta}{k \, T}$ $\ll 1$) and that the application to ζ - potentials larger than 25 mV as are frequently encountered in colloid chemistry leaves reason for doubt as to the quantitative validity. Nevertheless several important conclusions may be drawn.

1. The relaxation correction is not important (smaller than a few percent) for values of $\zeta \ll 25$ mV.

2. For very small values of $\varkappa \, a$ the relaxation correction may be neglected. However, these small values will practically never occur in colloids. The smallest value of $\varkappa$ is of the order of $10^5 (c = 10^{-5}$ mol/litre) and the smallest value of a of the order of 10^{-6} cm, so that $\varkappa \, a$ is practically always larger than 0.1.

3. For intermediate values of $\varkappa \, a$ (0.1–100) the relaxation effect may give important corrections if ζ is not very small. *This means that very often conclusions as to the value of ζ evaluated by electrophoretic measurements of colloids are open to serious doubt.*

4. For very large values of $\varkappa \, a$ the relaxation effect again becomes small. This has been proved by OVERBEEK in a more general way irrespective of the shape of the particle so that VON SMOLUCHOWSKI's equation (26) remains valid also if relaxation is taken into account.

In practice these cases of very thin double layer may be found in coarse colloids containing a great deal of electrolyte and generally in suspensions.

[1] D. C. HENRY, *Trans. Faraday Soc.*, 44 (1948) 1021.
[2] F. BOOTH, *Nature*, 161 (1948) 83, *Proc. Roy. Soc. London*, A 203 (1950) 514.

Conclusion 3 is especially important as it has been the custom for a long time to calculate ζ from electrophoresis experiments and it has been shown now that these values of ζ cannot be trusted.

Experimental evidence for the fourth conclusion can be found in the observations of FREUNDLICH and ABRAMSON [1] who found that the electrophoretic velocity of particles of quartz and other materials coated with egg albumin was independent of the shape
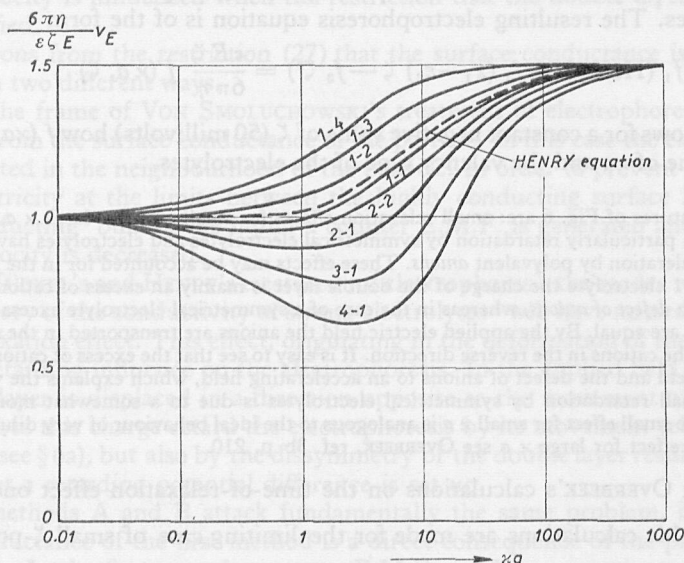
$$\frac{6\pi\eta}{\varepsilon\zeta E} v_E$$

Fig. 6.   The influence of the relaxation for different types of electrolytes on a negative particle. $\zeta = -50$ mV. The dotted line is HENRY's curve, calculated without taking account of the relaxation.

and the dimensions of the particles. As the particles used were all larger than 1 μ and the experiments carried out mostly in buffer solutions with $\varkappa > 10^6$ the condition $\varkappa a \gg 1$ was amply fulfilled.

A remarkable fact which is less easy to interpret is the fact that the electrophoretic velocity of pure egg albumin notwithstanding the smallness of the particles $(a = 2 \cdot 10^{-7}$ cm$)$ was found to be the same as that of the coated surfaces [2].

MOONEY [3], however, found that the electrophoretic velocity of oil droplets depended on the size of the droplets. If the droplets were covered with albumin the influence of the size disappeared. The explanation may perhaps be found in the special character of the double layer at an oil-water interface (*cf*. Chapter IV).

In the smaller droplets the double layer in the oil cannot develop to its full extent with a lowering of the ζ - potential as a consequence. Moreover electrophoretic motion within the oil phase may complicate the phenomena.

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[1] H. FREUNDLICH and H. A. ABRAMSON, *Z. physik. Chem.*, 128 (1927) 25; 133 (1928) 51, *cf*. ABRAMSON book, page 112.

[2] *cf*. J. TH. G. OVERBEEK, *Advances in Colloid Science* III, New York 1950, p. 129.

[3] M. MOONEY, *J. Phys. Chem.*, 35 (1931) 331; *Phys. Rev.*, (2) 23 (1924) 396.

ABRAMSON [1] and many other authors prefer to calculate the charge density σ instead of the ζ-potential from electrokinetic phenomena. In principle there is no objection against doing this but as the calculation of σ is often based upon the validity of the simplified DEBYE-HÜCKEL equations, in many cases the values of σ so found are not reliable [2]. Moreover we have seen [3] that in most cases the surface potential is a more fundamental characteristic of the interface than is its charge.

§ 7. EXPERIMENTAL METHODS FOR THE DETERMINATION OF THE ELECTROPHORETIC VELOCITY

a.   Introduction

Although it has been pointed out that experiments on electrophoresis are some-times difficult to interpret, they remain important in several respects. Firstly when the electrophoretic velocity is small, v is proportional to ζ and especially the zeropoint of electrophoretic velocity and thus of the ζ-potential can be determined accurately. Secondly when the double layer is thin, ζ can be evaluated with confidence and finally in the field of biocolloids electrophoretic velocity has been used to characterize different colloids (especially proteins) and has been applied as a means of separating them.

b.   The HITTORF method

The electrophoretic velocity may be determined in the same way as the transport number of an electrolyte. A certain current i is sent through a colloid during a time t, and the quantity of colloidal material (g) that has been displaced to anode or cathode is determined analytically. As the charge of a colloidal particle is relatively much smaller than that of an ion the mass of displaced material is comparatively large and this method of determination is fairly accurate [4].

The electrophoretic velocity. is given by

$$v_E = \frac{\lambda\, g}{cit} \tag{30}$$

when λ is the conductivity of the liquid and c the concentration of the colloid in grams/cm³.

The method, despite its advantages, has seldom been used. We cite only PAINE, PAULI, TATTJE [5].

The last named author used the HITTORF method not only to determine the electro-phoretic velocity but also in the same experiment the mobility of the counter ions.

[1] cf. ABRAMSON, book, page 107.

[2] cf. Chapter IV, page 129.

[3] cf. Chapter IV, page 126.

[4] A. TISELIUS in ABDERHALDEN's Handbuch der biologischen Arbeitsmethoden III B, Berlin 1929, p. 666; W. PAULI and E. VALKÓ, Elektrochemie der Kolloide, Vienna 1929, p. 160.

[5] H. H. PAINE, Trans. Faraday Soc., 24 (1928) 412; W. PAULI and L. ENGEL, Z. physik. Chem., 126 (1928) 247; P. TATTJE, Thesis, Utrecht 1941.

c. The moving boundary method

The observation of the displacement in an electric field of the boundary between a colloidal solution and the colloid-free dispersion medium offers another way of determining the electrophoretic velocity. A simple apparatus [1] for this method is represented in Fig. 7.

The lower part of the U-shaped tube is filled with the colloidal solution, the upper part with pure dispersion medium. When a potential difference is applied between the electrodes A and B, the boundaries are displaced and this movement can be measured fairly easily, allowing conclusions as to the sign of the charge and the electrophoretic velocity of the particles.

To avoid disturbances by reaction products generated at the electrodes it has been recommended [2] to put the working (current carrying) electrodes in side tubes and to use the electrodes A and B for measuring purposes only.

A more serious difficulty of this method is formed by the choice of the supernatant clear liquid. The first requirement which has to be met, is that during the electrophoresis the colloidal particles remain in a liquid of constant composition because this composition may influence the ζ-potential. The ultrafiltrate of the sol has been frequently used for this purpose. If however the conductivities of sol and ultrafiltrate are different (which is the case when the sol is relatively concentrated and the electrolyte content low) we get into other difficulties. Then the potential gradient in the U-tube shows discontinuous changes just at the place of the boundaries, where the electrophoresis has to be observed. KRUYT and VAN DER WILLIGEN (l.c.) indicated how this distribution of the electric field could be taken into account, but later

Fig. 7. Apparatus used by BURTON for the determination of the electrophoretic velocity by the moving boundary method.

discussions by various authors [3] showed that the difficulties are of a more fundamental nature.

As follows from the discussions, the moving boundary method can only give reliable results in two cases.

A.   The contribution of the colloidal particles to the electrical conductance may be neglected. In that case the ultrafiltrate (or a synthetic liquid having the composition of the ultrafiltrate) is the correct supernatant liquid. The particles remain always in the
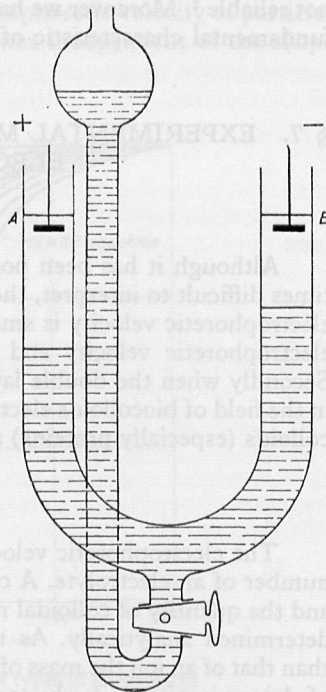
[1] E. F. BURTON, *Phil. Mag.*, (6) 11 (1906) 425; In a very simple form this method had already been used by H. PICTON and S. E. LINDER, *J. Chem. Soc.*, 61 (1892) 148.

[2] H. R. KRUYT and P. C. VAN DER WILLIGEN, *Kolloid-Z.*, 44 (1928) 22.

[3] W. HACKER, *Kolloid Beihefte*, 41 (1935) 147; *Kolloid-Z.*, 62 (1933) 37, 66; D. C. HENRY and J. BRITTAIN, *Trans. Faraday Soc.*, 29 (1933) 798; J. MUKHERJEE, *Kolloid-Z.*, 65 (1933) 297; G. S. HARTLEY, *Trans. Faraday Soc.*, 30 (1934) 648; C. ROBINSON and J. L. MOILLET, *Proc. Roy. Soc. London*, A 143 (1934) 630; J. L. MOILLET, B. COLLIE, C. ROBINSON, G. S. HARTLEY, *Trans. Faraday Soc.*, 31 (1935) 120.

same surroundings, and the potential gradient is constant so that the interpretation of the moving boundary method offers no difficulties.

This case has acquired a great significance in the hands of A. TISELIUS [1], whose electrophoretic apparatus is now widely used to follow the electrophoresis of proteins in pure preparation and in mixtures (see below § 7d).

B.   If the contribution of the particles to the conductance is not small but if the composition of the sol not only with respect to the number and the charge of the sol particles but also to that of the ionic components is exactly known, in favourable cases a suitable supernatant (colloid-free) liquid may be found either by calculation or by experiment.

As an example [2] the case of a sol consisting only of colloidal ions C^+ and an equivalent amount of counter ions A^- will be treated briefly. The colloid-free solution contains an electrolyte $M^+ A^-$ and is supposed to be above the boundary of Fig. 8. The electric field is applied in such a direction that the boundary descends. The solution M A has now to obey several conditions in order that this motion of the boundary be well defined and easy to follow. In order to avoid a mixing of the two solutions M^+A^- has to be the lighter of the two solutions. Furthermore the mobility of the ion M^+ has to be slower than that of the colloid ion C^+. This has a restoring effect on small disturbances in the neighbourhood of the boundary. If by diffusion an ion M^+ gets into the solution C^+A^- it will automatically lag behind and rejoin the original solution. Finally the concentration of M A has to be well adapted to that of the colloid so that the field strength in the upper solution is just so much larger than that in the lower one, that the difference in mobility of the ions C^+ and M^+ is exactly compensated.

Fig. 8. Moving boundary between a colloidal solution C^+ A^-. and a solution of an electrolyte M^+ A^-.

The number of conditions, which have to be satisfied, is so large that only in very simple cases can a solution be found and although the moving boundary method has given very accurate results in the case of electrolyte solutions the applicability to colloidal systems remains restricted [3].

d. The Tiselius method

Although the TISELIUS method is an application of the principle of the moving boundary (§ 7c) it contains so many special features that a separate treatment is completely justified.

This method has been developed from the apparatus of BURTON sketched in Fig. 7. In the first place the boundary between the sol and the colloid-free solution is made by shifting two parts of the electrophoresis vessel along each other. The lower part contains the sol and the upper part the clear solution (see Fig. 9).

Further the cross section of the electrophoresis tube is not round but rectangular giving far better possibilities of observation and a more intimate contact with the

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[1] A. TISELIUS, *The moving boundary method of studying the electrophoresis of proteins, Thesis,* Uppsala 1930; A. TISELIUS, *Svensk Kem. Tid.* 50 (1938) 58; A. TISELIUS, *Trans. Faraday Soc.,* 33 (1937) 524; A. TISELIUS, *Kolloid-Z.,* 85 (1938) 129.

[2] See for example D. A. MACINNES, *The principles of electrochemistry,* New York 1939, p. 69.

[3] *cf.* J. L. MOILLET, B. COLLIE, C. ROBINSON, and G. S. HARTLEY, *Trans. Faraday Soc.,* 31 (1935) 120, who applied this method to colloidal electrolytes of the paraffin chain salt type.
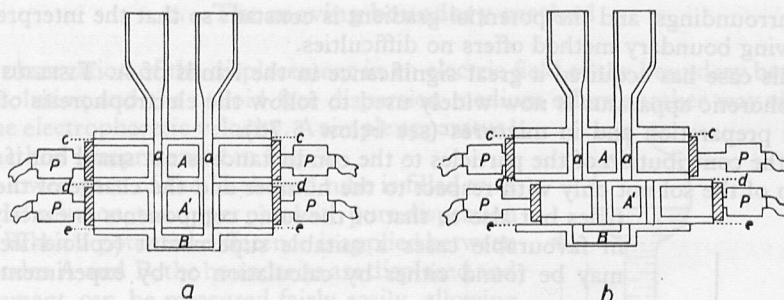
Fig. 9.   U-tube of TISELIUS apparatus, side view.

a. Working position.
b. Filling position for the upper part.
The lower part has already been filled with sol.

thermostat liquid so that greater current densities can be applied without setting up convection currents (Fig. 10).

The determinations are usually carried out near 4^0 C. where aqueous solutions have their maximum density. Consequently small temperature differences lead only to extremely small density differences with great benefit for the thermal stability.

The working electrodes are of the reversible (non-gassing) type and are placed in very large electrode vessels so that the danger of contamination of the sol by the electrode reaction products is avoided even in prolonged experiments (Fig. 11).
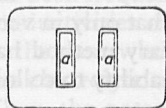

Fig.10. Horizontal cross-section through U-tube.

The supernatant colloid-free liquid is usually prepared by dialysis. See on this point however the remarks made in § 7c, p. 214.

Finally the observational technique has been greatly improved. The wish to determine the electrophoretic velocity of proteins and other non-coloured

Fig. 11.   Complete electrophoresis apparatus.

solutions required a method not based upon colour differences. Nowadays the observations are usually carried out with the aid of the "Schlieren" method of TOEPLER in one of its modern modifications [1] or with the more accurate but also more time-consuming scale method [2]. These methods of observation are based upon the difference in refractive index of the two solutions.
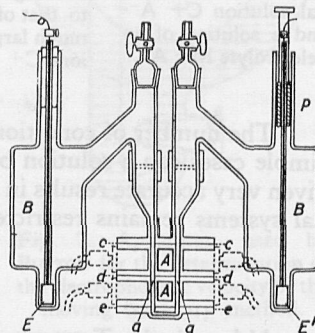
In Fig. 11 a parallel light beam is sketched which passes through a solution with a concentration gradient in it. This concentration gradient involves a gradient of the refractive index. The wave front

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[1] J. St. L. PHILPOT, *Nature*, 141 (1938) 283; L. G. LONGSWORTH, *Ann. N. Y. Acad. Sci.*, 39 (1939) 188; *Ind. Eng. Chem. Anal. ed.* 18 (1946) 219; L. G. LONGSWORTH, and D. A. MacINNES, *Chem. Revs.* 24 (1939) 271; H. SVENSSON, *Kolloid-Z.*, 87 (1939) 181; *Arkiv Kemi Mineral. Geol.*, 22 (1946) No. 10.
[2] O. LAMM, *Nova Acta Regiae Soc. Sci. Upsaliensis*, 10 (1937) no. 6.

of the rays which passes through the gradient and which is vertical before the cell is passed changes gradually into a more inclined position. When the beam has passed the cell, rays passing the gradient region are now directed downwards, the angle they make with the horizontal being a measure of the refractive index gradient. The further observation of the diverted beam is different in the different
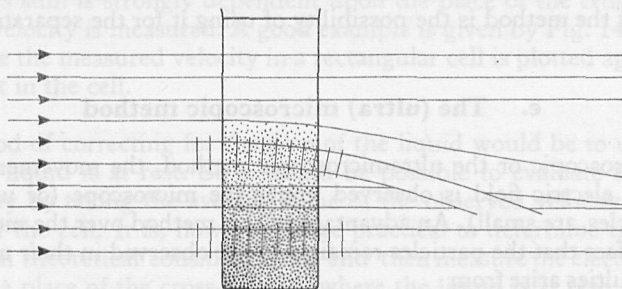

Fig. 12. Horizontal light beam falling on a cell with a horizontal
concentration gradient. In the middle rays the direction of the wave
fronts has been indicated.

methods. In the PHILPOT-SVENSSON method (Fig. 13) an inclined slit is placed in the plane of the normal and the deviated image of the light source. The undeviated light passes through this slit at A. The deviated images are the more in front of A the more they have been deviated. Now with the help of a spherical and a cylindrical lens the cell *and* the inclined slit are both imaged on the photographic plate.
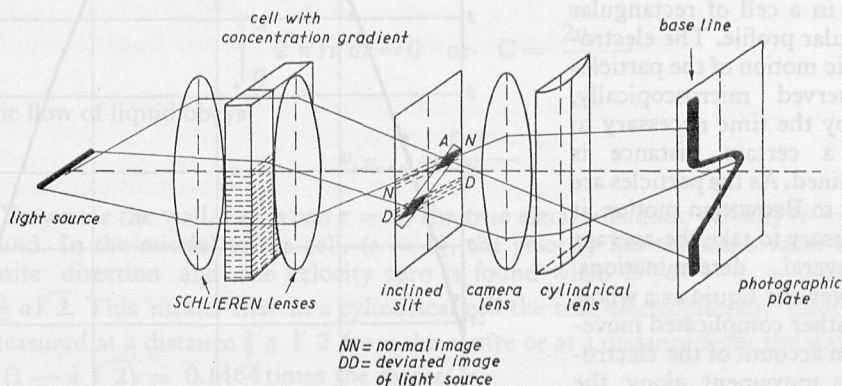

Fig. 13. Sketch of diagonal slit "Schlieren" method.

As a cylindrical lens is present in the light path it is impossible that both horizontal and vertical image of the same object are sharp. The focussing is now chosen in such a way that horizontal lines from the cell but vertical lines from the plane of the inclined slit are truly pictured.

In the photographic plate therefore the vertical ordinate gives a measure of the place in the cell, the horizontal one a measure of the refractive index gradient.

When no refractive index gradient is present the picture consists of one vertical line (the base line). A gradient is indicated by a hump in the curve, the place of the maximum of this hump being a measure for the position of the boundary, the narrowness of the hump a measure of the sharpness of the boundary and the surface under the hump a measure for the concentration difference on both sides of the boundary.

The same method of observation can be used in diffusion measurements and in sedimentation measurements with the ultracentrifuge.

The TISELIUS method of determining electrophoresis has been especially impor-
tant in the investigation of proteins and other hydrophilic colloids. One of its essential
features is the possibility of determining electrophoresis in a mixture of different pro-
teins. The Schlieren picture then contains two or more different humps. Another inter-
esting feature of the method is the possibility of using it for the separations of mixtures
of proteins.

e.   The (ultra) microscopic method

In the microscopic or the ultramicroscopic method, the movement of individual
particles in the electric field is observed under the microscope (or ultramicroscope,
when the particles are small). An advantage of this method over the moving boundary
method is the fact that the particles remain and are observed in their natural surroun-
dings. No difficulties arise from
the complicated conditions at
the separation plane of sol and
colloid-free liquid. Another ad-
vantage of the microscopic
method consists in the small
quantities of colloidal solution
necessary for a determination.

The colloidal solution is
placed in a cell of rectangular
or circular profile. The electro-
phoretic motion of the particles
is observed microscopically,
whereby the time necessary to
cover a certain distance is
determined. As the particles are
subject to BROWNian motion, it
is necessary to take the average
of several determinations.
Moreover the liquid as a whole
has a rather complicated move-
ment on account of the electro-
osmotic movement along the
walls of the cell. This electro-
osmotic movement tries to dis-
place the liquid in the direction
of one of the electrodes, thereby
generating a difference of pres-
sure between the extremities of
the cell. As a consequence of
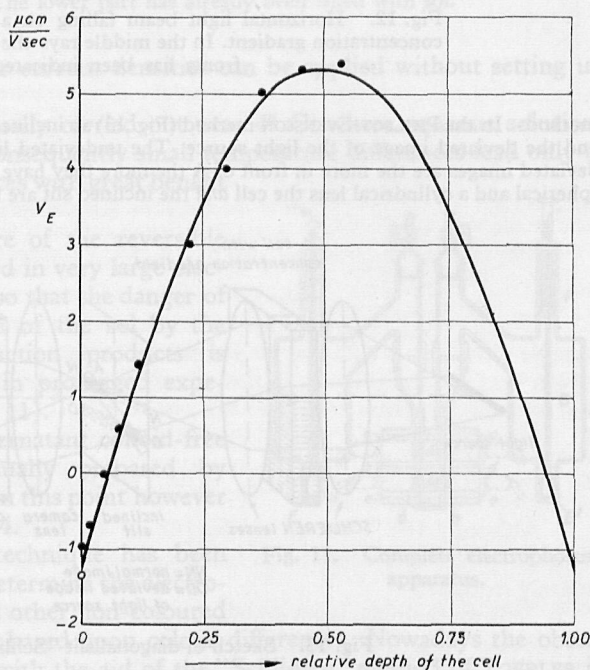this pressure difference a re-

Fig. 14.   Observed velocity of oil droplets at different depths
of the cell. The drawn parabola corresponds to the theoretical
equation (33) with an electrophoretic velocity of $3.18 \cdot 10^{-4}$
cm^2/V. sec. and an electro-osmotic velocity of $4.50 \cdot 10^{-4}$
$cm^2/V.sec.$

turn flow of liquid exists, obeying the laws of laminar flow. In the stationary state,
the total transport of liquid must be zero, by a balancing of the two flows mentioned
above. This does not imply, however, that the liquid is at rest everywhere, because
the return flow is strong in the middle of the cross-section and weak near the walls

of the cell, whereas the electro-osmotic flow has a constant velocity all over the cell [1].

This velocity of the liquid is superimposed on the electrophoretic velocity of the particles and the only thing that can be measured directly is the sum of the two. Now the value of this sum is strongly dependent upon the place of the cross-section of the cell where the velocity is measured. A good example is given by Fig. 14, from the work of ELLIS [2] where the measured velocity in a rectangular cell is plotted against the height of measurement in the cell.

One method of correcting for the flow of the liquid would be to use the fact that as a whole the liquid is at rest. So it would be possible to evaluate the true electrophoretic velocity by taking the average value of the observed velocity over the whole cross-section of the cell. It is, however, more practical to determine the profile of the liquid flow from theoretical considerations, and then measure the electrophoretic velocity directly at a place of the cross-section, where the liquid is at rest.

For a cylindrical cell with a radius a this place may be determined as follows. The velocity of the liquid, being the sum of a constant electro-osmotic flow, $v_{e \cdot o \cdot}$, and a return flow following the law of POISEUILLE, is given by

$$v = v_{e \cdot o \cdot} - C (a^2 - r^2) \tag{31}$$

where r is the distance from the axis of the cylinder, and C a constant.

The value of C is determined by the condition that the total flow through a cross-section must be zero, or

$$\int_0^a 2 \pi r v \, dr = 0 \quad \text{or} \quad C = \frac{2v_{e \cdot o \cdot}}{a^2}$$

So the flow of liquid obeys

$$v/v_{e \cdot o \cdot} = \frac{2 r^2}{a^2} - 1 \tag{32}$$

Very near the wall, *i.e.*, when $r = a$, the true electro-osmotic velocity ($v = v_{e \cdot o \cdot}$) is found. In the middel of the cell, ($r = 0$), the velocity has the same value but the opposite direction and the velocity zero is found when $2r^2/a^2 - 1 = 0$ or when $r = \frac{1}{2} a \sqrt{2}$. This means that in a cylindrical cell the true electrophoretic velocity can be measured at a distance $\frac{1}{2} a \sqrt{2}$ from the centre or at a distance from the wall equal to $\frac{1}{2} (1 - \frac{1}{2} \sqrt{2}) = 0.1464$ times the diameter.

In very much the same way the profile of the flow and the place where this flow is zero in a rectangular cell can be calculated. When the depth of the cell is d, and the distance from the top or bottom h, equation (32) is replaced by (33) for an infinitely large cell.

$$v/v_{e \cdot o \cdot} = 1 - 6 \left(\frac{h}{d} - \frac{h^2}{d^2} \right) \tag{33}$$

In such a cell $v = 0$ when $h/d = 0.2113$. In a cell with a finite breadth (b) the profile is

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[1] In the moving boundary method the same complications would arise. Only in this case the return flow caused by the pressure has a practically constant value over the whole cross section if the U-tube used is sufficiently wide.

[2] R. ELLIS, *Z. physik. Chem.*, 78 (1912) 321.

more complicated and the distance from the wall where $v = 0$ depends on the ratio of breadth and depth of the cell. (On the supposition that the measurement is carried out in the middle of the breadth).

Table 1 [1] shows that as soon as the cell is not extremely flat ($b/d < 20$) the value of h where $v = 0$ deviates markedly from the value for $b = \infty$.

TABLE 1

$h_0 =$ height where the liquid is at rest in a rectangular electrophoresis cell.

$d =$ total depth of the cell. $b =$ breadth of the cell.

b/d	h_0/d
3.183	0.162
10.0	0.194
20.0	0.202
50.0	0.208
∞	0.2113

For accurate measurements it is always necessary to determine if the liquid motion is symmetrical around the axis of the cell, especially if rectangular cells are used cemented together from plateglass, because in this case a difference between the top and bottom plates may introduce serious dissymmetries.

The microscopic method, apart from giving a value for the electrophoretic velocity can also be used to determine the electro-osmotic velocity. The movement of the liquid, as described by the eq. (32) or (33) cannot be measured directly but if the liquid contains particles in suspension and if the movement of these *particles* is determined for at least two different heights the velocity of the electro-osmosis may be evaluated. In the circular cell for instance

$$v_{e.o.} = v_{r=a} - v_{r=\frac{1}{2}a\sqrt{2}}$$

or

$$v_{e.o.} = v_{r=\frac{1}{2}a\sqrt{2}} - v_{r=0}$$

This last equation especially offers an accurate way of determining the electro-osmotic velocity.

Microscopic measurements of electrophoresis have been carried out in a number of different ways. One of the more standard types [2] of cells is sketched in Fig. 15. This cell, frequently used in biochemical work, contains reversible electrodes (zinc rods in saturated $ZnSO_4$).

The field strength is determined either with the help of measuring electrodes in the middle part of the cell or by calculation from the current, the conductivity of the liquid and a cell constant.

A cylindrical cell based upon the same principle has been developed by MATTSON [3], who used a thick-walled capillary ground flat at the place of observation.

Another type of cylindrical cell has been described by VAN GILS and KRUYT [4] and improved by TROELSTRA and KRUYT [5]. This cell using a thin walled glass capillary allows

[1] J. ALLEN, *Phil. Mag.*, 18 (1934) 488; S. KOMAGATA, *Researches Electrotech. Lab. Tokyo*, Comm. No. 348 (1933).
[2] H. A. ABRAMSOM, *J. Gen. Physiol.*, 12 (1929) 469; *J. Phys. Chem.*, 36 (1932) 1454. J. H. NORTHROP and M. KUNITZ, *J. Gen. Physiol.*, 7 (1925) 929.
[3] S. MATTSON, *J. Phys. Chem.*, 37 (1933) 223.
[4] G. E. VAN GILS and H. R. KRUYT, *Kolloid-Beihefte*, 45 (1936) 60.
[5] S. A. TROELSTRA and H. R. KRUYT, *Kolloid-Z.*, 101 (1942) 182.

a very accurate control of the temperature. This cell allows greater accuracy than that of MATTSON, except when the concentration of the electrolyte is high, because the "VAN GILS" cell does not contain reversible electrodes.

In the foregoing it has been assumed that the particles whose electrophoretic mobility is to be measured can be made visible either in the microscope or in the ultra-
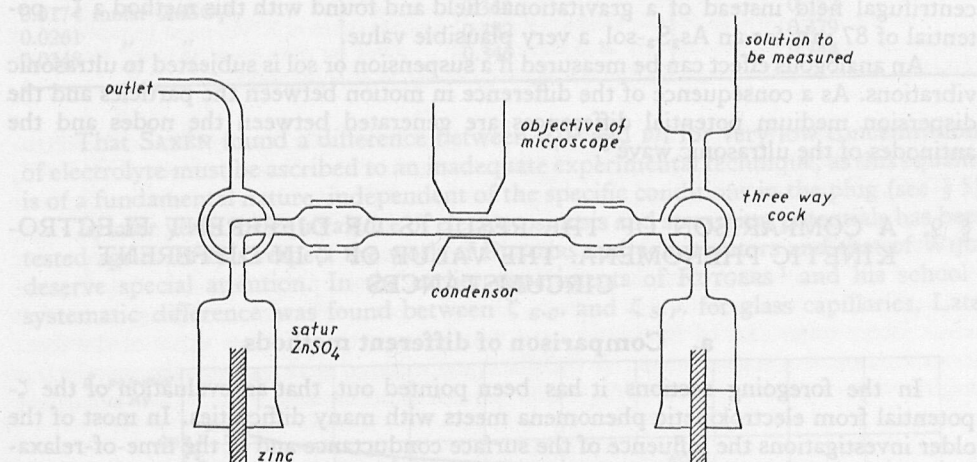

Fig. 15. Micro-electrophoresis cell.

microscope. Consequently the method seems to be inapplicable to hydrophilic sols, where the particles cannot be observed separately. Nevertheless even in this case the microscopic method can often be applied when the hydrophilic colloid is adsorbed on small particles, for example, of quartz or carbon. The electrophoretic mobility of these (easily visible) adsorption complexes appears often to be the same as that of the free colloids (*cf.* § 6b, p. 212 of this chapter and Ch. VII of vol. II).

§ 8.   POTENTIALS OF MOVING PARTICLES

The potential differences caused by the movement of particles through a liquid have only been investigated very rarely and rather superficially. The technique is difficult and it is not to be expected that the experiments will give additional information to the results of the other electrokinetic phenomena. We mention here the experiments of DORN [1], BILLITER [2], MÄKELT[3] and STOCK [4], the last of which could confirm VON SMOLU-CHOWSKI's [5] equation for this phenomenon.

$$E = \frac{\varepsilon\,\zeta}{3\,\eta\,\lambda}\,r^3\,(\delta - \delta')\,ng \tag{34}$$

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[1] E. DORN, *Wied. Ann.*, 10 (1880) 70.

[2] J. BILLITER, *Ann. Physik*, (4) 11 (1903) 937.

[3] H. FREUNDLICH and E. MÄKELT, *Z. Elektrochem.*, 15 (1909) 161.

[4] J. STOCK, *Bull. intern. acad. sci. Cracovïc*, A (1913) 131; (1914) 95.

[5] M. VON SMOLUCHOWSKI, *Graetz Handbuch der Elektrizität und des Magnetismus* II, Leipzig 1921, p. 385

where r is the radius of the falling spheres, n their concentration, δ and δ' the density of the spheres and of the liquid, η the viscosity, λ the specific conductivity and g the gravitational constant.

A later investigation of BURTON and CURRIE [1] with shot falling through water and organic liquids is again only of a qualitative character.

Recently the method has been taken up again by RUTGERS and JACOBS [2] who used a centrifugal field instead of a gravitational field and found with this method a ζ - potential of 87 mV for an As_2S_3-sol, a very plausible value.

An analogous effect can be measured if a suspension or sol is subjected to ultrasonic vibrations. As a consequence of the difference in motion between the particles and the dispersion medium potential differences are generated between the nodes and the antinodes of the ultrasonic wave [3].

§ 9. A COMPARISON OF THE RESULTS OF DIFFERENT ELECTRO-KINETIC PHENOMENA. THE VALUE OF ζ IN DIFFERENT CIRCUMSTANCES

a. Comparison of different methods

In the foregoing sections it has been pointed out, that an evaluation of the ζ-potential from electrokinetic phenomena meets with many difficulties. In most of the older investigations the influence of the surface conductance and of the time-of-relaxation effect has not been fully distinguished. So, although there exists a great number of investigations on electrokinetics, only relatively few can be accepted as a basis for computing ζ-potentials. In order to ascertain whether the notion of ζ has got a base in reality, it will have to be verified if identical values for the ζ-potential are found, irrespective of whether it has been evaluated from electrophoresis, electro-osmosis or streaming-potential.

a. 1. Electro-osmosis and streaming potential

In the first place electro-osmosis may be compared with streaming potentials. In this case identical conditions at the interface can be provided without difficulties by the use of one apparatus where the same liquid and the same diaphragm is used for the two experiments. It follows from § 5 eq. 24 that E/P has to be equal to v/i, both being equal to $\varepsilon \zeta/4 \pi\eta\lambda$ when surface conductance is absent. This equality has already been tested by SAXÉN [4] who could confirm it for relatively concentrated solutions. For pure water, however, he found deviations from equality. Some results of SAXÉN are shown in table 2 giving values of E/P from streaming potentials and v/i from electro-osmosis for the same diaphragm of clay.

[1] E. F. BURTON and J. C. CURRIE, Phil. Mag., (6) 49 (1925) 194.
[2] G. JACOBS, Mededeel. Koninkl. Vlaam. Acad. Wetenschap. Belg. Klasse Wetenschap., 7 (1945) no. 4; A. J. RUTGERS, Nature, 157 (1946) 74.
[3] P. DEBYE, J. Chem. Phys., 1 (1933) 13; J. J. HERMANS, Phil. Mag. (7) 26 (1938) 674; A. J. RUTGERS, Physica, 5 (1938) 46; A. J. RUTGERS, Nature, 157 (1946) 74; J. VIDTS, Mededeel. Koninkl. Vlaam. Acad. Wetenschap. Belg. Klasse Wetenschap., 7 (1945) no. 3.
[4] U. SAXÉN, Wied. Ann., 47 (1892) 46.

TABLE 2

COMPARISON OF ELECTRO-OSMOSIS AND STREAMING POTENTIALS

Solution	v/i	E/P
0.0174 molar ZnSO$_4$	0.360	0.352
0.0261 ,, ,,	0.382	0.379
0.0348 ,, ,,	0.346	0.344

That SAXÉN found a difference between E/P and v/i for very low concentrations of electrolyte must be ascribed to an inadequate experimental technique, as this equality is of a fundamental nature, independent of the specific conditions in the plug (see § 5).

In later years the equivalence of electro-osmosis and streaming potentials has been tested again. In this respect the work of RUTGERS and collaborators and that of WIJGA deserve special attention. In the earlier experiments of RUTGERS [1] and his school a systematic difference was found between $\zeta_{E.O.}$ and $\zeta_{S.P.}$ for glass capillaries. Later
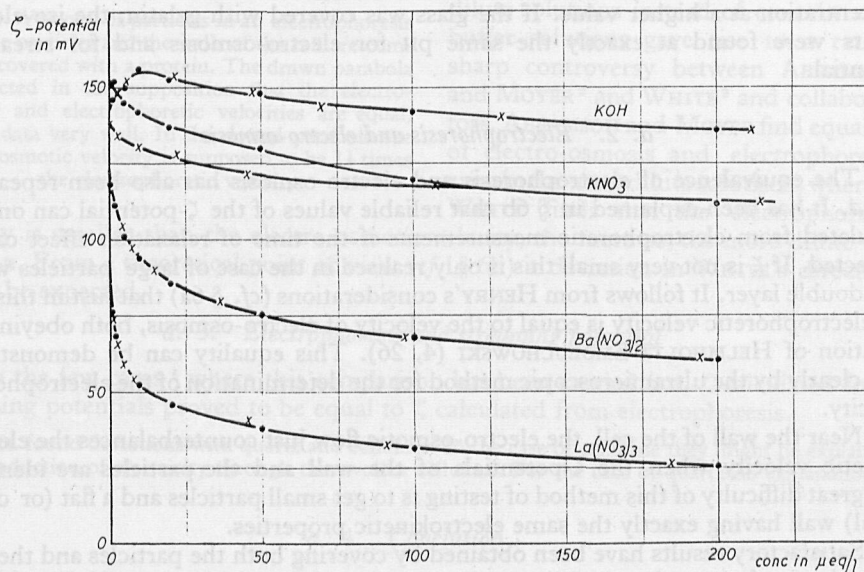

Fig. 16. ζ-potentials of pyrex glass evaluated from electro-osmosis (•) and from streaming potentials (×) as a function of the concentration of electrolyte. The data for KNO$_3$ derived from electro-osmosis should probably be disregarded owing to a different treatment of the capillary, as in this case the water value ($c = 0$) is abnormally high.

[1] A. J. RUTGERS, E. VERLENDE, and MA. MOORKENS, Proc. Acad. Sci. Amsterdam, 41 (1938) 763; E. VERLENDE, Proc. Acad. Sci. Amsterdam, 42 (1939) 764; A. J. RUTGERS, Trans. Faraday Soc., 36 (1940) 69; M. DE SMET, Mededeel. Koninkl. Vlaam. Acad. Wetenschap. Belg. Klasse Wetenschap.. 3 (1941) no. 12, 14; 4 (1942) no. 4, 8.

experiments [1] of the same school of investigators showed, however, a complete accord between electro-osmosis and streaming-potentials.

In Fig. 16, taken from WIJGA's work [2], the ζ-potentials of a glass capillary in contact with solutions of electrolyte have been plotted against the concentration. The values found with streaming potentials (crosses) and with electro-osmosis (dots) fall on the same curve.

The deviations between the two methods for small concentrations of KNO_3 must be explained by different treatments of the capillary as in this case the ζ - value for pure water as found by electro-osmosis was abnormally large (153 mV against 137-140 mV in all other cases).

MONAGHAN, WHITE and URBAN [3] who determined the zero-points of electro-osmosis and of streaming potential of glass in contact with solutions of salts like $AlCl_3$ or $ThCl_4$, reversing the sign of the charge, found a difference between electro-osmosis and streaming potentials, in this respect, that the zero-point was reached for a lower concentration in streaming potentials than in electro-osmosis. The explanation probably is that these solutions contain such a small quantity of the polyvalent ion that they are not sufficiently buffered in this respect. In the experiments on streaming potentials much larger quantities of liquid are used which keeps the effective value of the ionic concentration at a higher value. If the glass was covered with gelatin, the iso-electric points were found at exactly the same pH for electro-osmosis and for streaming potential.

a. 2.   Electrophoresis and electro-osmosis

The equivalence of electrophoresis and electro-osmosis has also been repeatedly tested. It has been explained in § 6b that reliable values of the ζ-potential can only be calculated from electrophoretic measurements if the time-of-relaxation effect can be neglected. If ζ is not very small this is only realised in the case of large particles with a thin double layer. It follows from HENRY's considerations (*cf.* § 6a) that just in this case the electrophoretic velocity is equal to the velocity of electro-osmosis, both obeying the equation of HELMHOLTZ-SMOLUCHOWSKI (4, 26). This equality can be demonstrated very clearly by the ultramicroscopic method for the determination of the electrophoretic velocity.

Near the wall of the cell, the electro-osmotic flow just counterbalances the electrophoretic velocity when the ζ-potentials of the wall and the particles are identical. The great difficulty of this method of testing is to get small particles and a flat (or cylindrical) wall having exactly the same electrokinetic properties.

Satisfactory results have been obtained by covering both the particles and the wall with a layer of a protein which is readily adsorbed thereon and makes them as far as electrokinetics are concerned absolutely equal. The concentration of protein in the liquid necessary to reach a complete covering is often astonishingly small ($\infty 0.01\%$).

[1] M. DE SMET, *Mededeel. Koninkl. Vlaam. Acad. Wetenschap. Belg. Klasse Wetenschap.*, 7 (1945) no. 5; A. J. RUTGERS and M. DE SMET, *Trans. Faraday Soc.*, 43 (1947) 102.

[2] P. W. O. WIJGA, *Thesis*, Utrecht 1946.

[3] B. MONAGHAN, H. L. WHITE, and F. URBAN, *J. Phys. Chem.*, 39 (1935) 585; *cf.* also R. DUBOIS and A. H. ROBERTS, *J. Phys. Chem.*, 40 (1936) 5, 43.
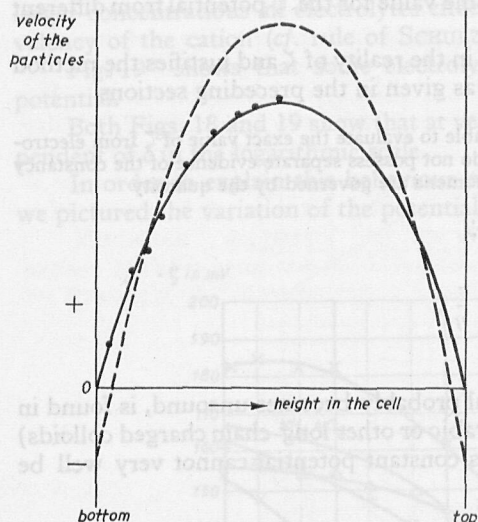
Fig. 17. Velocity of particles in an electrophoresis cell. The particles and the walls of the cell are completely covered with a protein. The drawn parabola constructed in the supposition that the electro-osmotic and electrophoretic velocities are equal, fits the data very well. In the dotted parabola the electro-osmotic velocity is supposed to be $1\frac{1}{2}$ times the electrophoretic velocity.

Fig. 17 shows a plot of the velocity of the particles in an electrophoresis cell, covered with a protein.

There is no doubt that the velocity of the particles, when extrapolated to the top and bottom of the cell, would be zero, thereby demonstrating the equality of the electrophoresis and electro-osmosis [1].

In Fig. 17 the dotted parabola has been constructed for an electro-osmotic velocity $1\frac{1}{2}$ times as large as the electrophoretic velocity. This ratio is expected if the electrophoresis is described by HÜCKEL's equation, $v = \varepsilon \zeta / 6 \pi \eta$ and the electro-osmosis by SMOLUCHOWSKI's equation, $v = \varepsilon \zeta / 4 \pi \eta$.

The same sort of experiments with dilute solutions instead of concentrated buffer solutions gave rise to a rather sharp controversy between ABRAMSON and MOYER [2] and WHITE [3] and collaborators. ABRAMSON and MOYER find equality of electro-osmosis and electrophoresis even in the most dilute solutison, whereas WHITE finds that the electrophoretic velocity is smaller than the electro-osmotic velocity, the more so, the more dilute the solution. From a theoretical point of view (cf. § 6b) a deviation in WHITE's direction would be expected.

a. 3. Electrophoresis and streaming potential

In the few cases [4] where this comparison has been carried out, ζ calculated from streaming potentials proved to be equal to ζ calculated from electrophoresis.

BULL found deviations with quartz and cellulose. In the case of cellulose they might be explained by a conduction of electricity through the swollen cellulose. For the case of quartz no explanation is offered.

a. 4. Conclusion

Although the material is anything but abundant, and not in all points absolutely conclusive, we may nevertheless conclude that the three electrokinetic phenomena are

[1] ABRAMSON, book pg. 120; H. A. ABRAMSON, *J. Gen. Physiol.*, 16 (1932) 1; H. A. ABRAMSON and L. S. MOYER, *J. Gen. Physiol.*, 19 (1936) 727. L. S. MOYER, *J. Phys. Chem.*, 42 (1938) 71, 391.

[2] H. A. ABRAMSON and L. S. MOYER, *J. Gen. Physiol.*, 19 (1936) 727; L. S. MOYER, *J. Phys. Chem.*, 42 (1938) 71, 391.

[3] H. L. WHITE, B. MONAGHAN, and F. URBAN, *J. Phys. Chem.* 39 (1935) 611, 925; H. L. WHITE and L. FOURT, *J. Phys. Chem.*, 42 (1938) 29.

[4] D. R. BRIGGS, *J. Am. Chem. Soc.*, 50 (1928) 2358; H. A. ABRAMSON, *J. Am. Chem. Soc.*, 50 (1928) 390; H. B. BULL, *J. Phys. Chem.*, 39 (1935) 577.

all equivalent, and allow us to evaluate a same value for the ζ-potential from different experiments.

This emphatically strengthens our belief in the reality of ζ and justifies the method of approach to the electrokinetic phenomena as given in the preceding sections.

This does not imply, however, that we are now able to evaluate the exact value of ζ from electro-kinetics. There remains an incertainty as long as we do not possess separate evidence of the constancy of ε and η in the double layer. All electrokinetic phenomena are governed by the quantity

$$\int \frac{\varepsilon}{\eta} \, d\psi$$

which can only be simplified to

$$\frac{\varepsilon}{\eta} \int d\psi = \frac{\varepsilon}{\eta} \zeta$$

if ε and η are considered as constants.

A case where the notion of the ζ-potential probably becomes unsound, is found in the electrophoresis of macromolecules (gum arabic or other long-chain charged colloids) where the slipping plane with a more or less constant potential cannot very well be imagined.

b. Examples of ζ-potentials

b. 1. *Glass-water interface*

Very extensive researches have been carried out on the ζ-potential of the interface glass-water. Glass has a great many advantages for this work. It exists in plate-form, as diaphragms, as fine powder; capillaries can be made of it. The possibilities of using it as a glass-electrode can give information about the variations of the total potential drop (ε-potential) between the two phases. From a chemical point of view there are some disadvantages too (intricate composition, lack of definition, extraction of the surface layer by prolonged contact with water) but most authors have taken these into the bargain.

Owing to the chemical differences no two researches in this field can be compared quantitatively although as a rule there is a good agreement in a qualitative way.

A typical result [1] is shown in Fig. 16 from WIJGA's [2] work on electro-osmosis and streaming potentials.

If ζ is plotted against the logarithm of the concentration straight lines have been found in many cases. Thus ζ can be represented by

$$\zeta = A - B \log c \qquad (35)$$

Figures 16 and 18 [3] clearly show the different influences on the ζ-potential. OH⁻ and H⁺-ions are potential-determining ions. So a small increase of OH⁻-ions increases the (negative) ζ-potential whereas H⁺-ions make it decrease. For somewhat

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[1] In older investigations often not only the curve for KOH but also those for other electrolytes show a maximum for low concentrations. This effect, the depression of ζ for very low concentrations, however, has to be ascribed to not taking account of the surface conductance, which has a tendency to lowering the values of E/P especially for dilute solutions.

[2] P. W. O. WIJGA, *Thesis*, Utrecht 1946.

[3] *cf.* A. J. RUTGERS, and M. DE SMET, *Trans. Faraday Soc.*, 41 (1945) 758.

larger concentrations all electrolytes effect a decrease of ζ, the more so, the larger the valency of the cation (*cf.* rule of SCHULZE and HARDY, Ch. VIII).

Fig. 19 [1] shows that some electrolytes are capable of reversing the sign of the ζ-potential.

Both Figs. 18 and 19 show that at very low concentrations ζ becomes nearly independent of c in the logarithmic scale.

In order to explain this behaviour of ζ qualitatively, Fig. 20 may be useful. In it we pictured the variation of the potential with distance from the wall (*cf.* Ch. IV) and
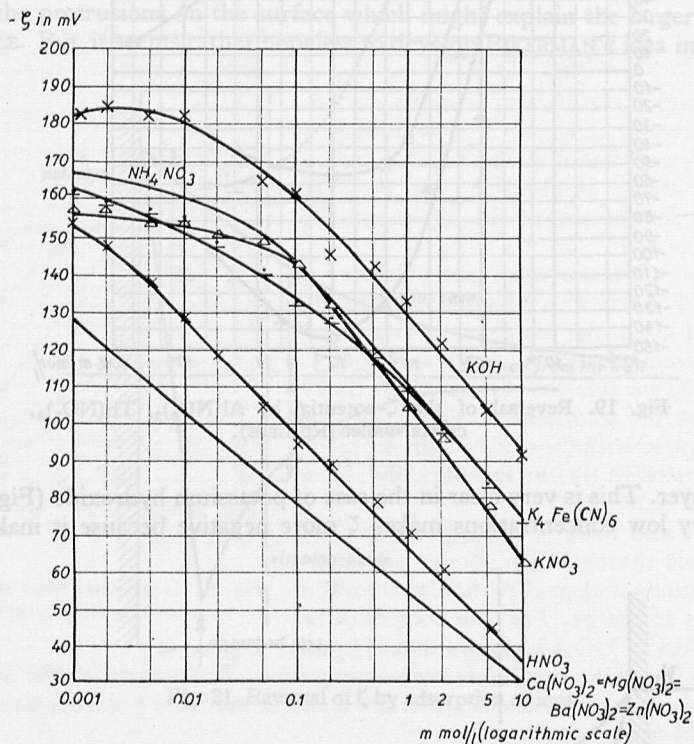

Fig. 18. ζ against log c. Taken from work of RUTGERS.

at a certain distance from the wall the slipping-plane is drawn, where the potential is equal to ζ. The curves 1 and 2 represent two cases with the same total potential (same concentration of potential-determining electrolytes) but the electrolyte content for curve 2 is much higher than that for curve 1. It is clear that ζ is decreased by addition of electrolytes and that the influence of higher charged counterions is much greater than that of ions of lower charge because the latter have less influence on the thickness of the double layer. The effect of the potential-determining electrolytes is twofold. In the first place they change ψ_0 and secondly they work like any electrolyte in compressing

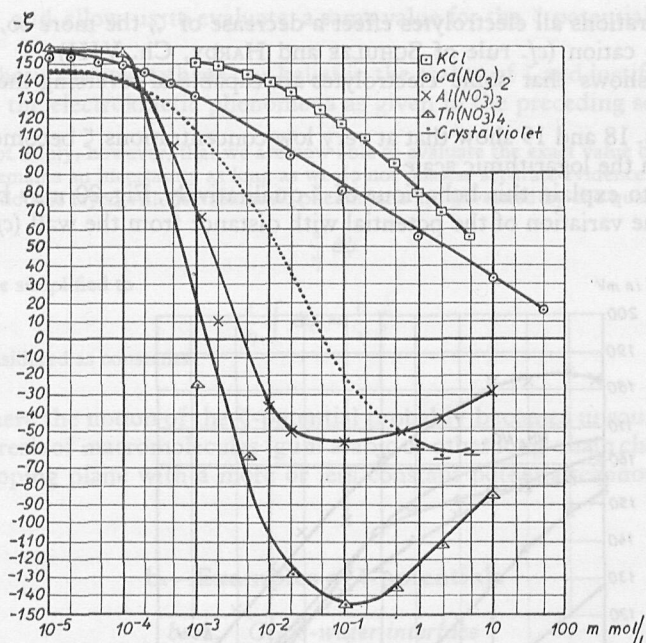[1] A. J. RUTGERS and M. DE SMET, *Trans. Faraday Soc.*, 41 (1945) 764.

Fig. 19. Reversal of the ζ-potential by $Al(NO_3)_3$, $Th(NO_3)_4$, crystal-violet (RUTGERS).

the double layer. This is very clear in the case of potassium hydroxide (Fig. 16 and 18) which in very low concentrations makes ζ more negative because it makes ψ_0' more
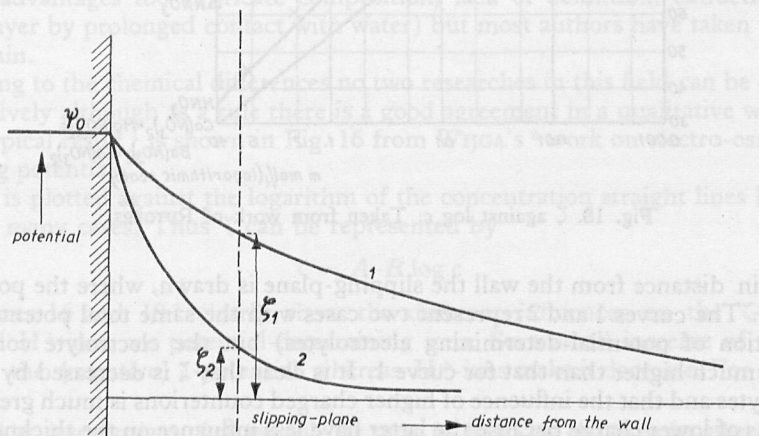

Fig. 20. Distribution of potential in the double layer. ψ_0 and ζ potentials.

negative, but in somewhat higher concentrations the effect of compressing the double layer prevails.

Nevertheless if one tries to draw more quantitative conclusions from this picture difficulties are still present. EVERSOLE and BOARDMAN [1] for instance calculate the distance (t) between the slipping-plane and the interface from the $\zeta - c$ relation found by different investigators. They assume a double layer of the GOUY type with a suitable value of ψ_0. In many cases the results can be explained by a constant value of t, this value however, differing from one series of experiments to another, between 8 and 100 Å. It cannot be denied that these values seem rather high to allow for a satisfactory molecular image of the situation of the slipping-plane.

BIKERMAN [2] suggested that the slipping-plane should be a sort of enveloping surface of the protrusions on the surface which might explain the larger values found by EVERSOLE. But it seems rather hopeless to develop BIKERMAN's idea into a quantita-
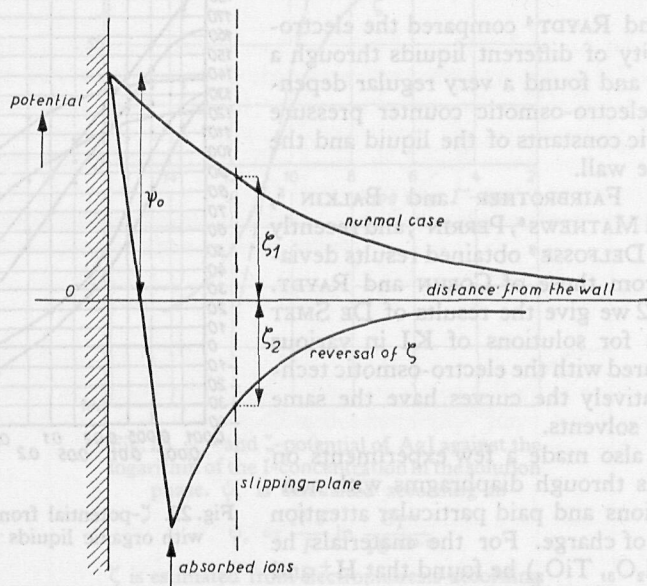

Fig. 21. Reversal of ζ by adsorption of ions.

tive theory. A possibility that has not yet been fully tried out is the application of the STERN-GOUY picture of the double layer with the assumption that slipping plane and separation between STERN and GOUY layer coincide. For very small concentrations this picture would lead to a near identity of ψ_o and ζ and thus explain that at these low concentrations electrolytes have no influence on ζ except the potential-determining ones HNO_3 and KOH. At higher concentrations the compression of the GOUY double layer would explain the lowering of ζ.

The special differences between different electrolytes of the same valency and the reversal of charge by strongly adsorbed electrolytes would enter easily into the same picture as a consequence of STERN's adsorption potentials.

[1] W. G. EVERSOLE and W. W. BOARDMAN, *J. Chem. Phys.*, 9 (1941) 789.
[2] J. J. BIKERMAN, *J. Chem. Phys.*, 9 (1941) 880.

It is known from experiments with the glass-electrode [1] that these electrolytes (Al salts, Th salts, crystal violet etc.), however strongly they influence ζ, have no effect on the total potential drop. The reversal of ζ can thus only be explained by a complicated variation of the potential in the double layer. This variation, represented schematically in Fig. 21 must be caused by a strong adsorbability [2] of the ions in question or of the products of their hydrolysis [3]. The adsorbed layer must bear a larger charge than is present on the wall, so that in the outer part of the double layer the charge (and the potential) must be reversed in order to maintain electro-neutrality.

b. 2. Organic liquids

COEHN and RAYDT [4] compared the electro-osmotic velocity of different liquids through a glass capillary and found a very regular dependence of the electro-osmotic counter pressure on the dielectric constants of the liquid and the material of the wall.

However FAIRBROTHER and BALKIN [5], STRICKLER and MATHEWS [6], PERRIN [7], and recently DE SMET and DELFOSSE [8] obtained results deviating widely from those of COEHN and RAYDT.

In Fig. 22 we give the results of DE SMET and DELFOSSE for solutions of KI in various solvents measured with the electro-osmotic technique. Qualitatively the curves have the same aspects for all solvents.

VERWEY [9] also made a few experiments on electro-osmosis through diaphragms with non-aqueous solutions and paid particular attention to zero points of charge. For the materials he used (SiO_2, Al_2O_3, TiO_2) he found that H^+ and

Fig. 22. ζ-potential from electro-osmosis with organic liquids against glass.

OH^- ions behaved as potential-determining ions. The nature of the liquid was of influence on the zero-point of charge. Water and acetone cause a more negative potential than methanol and ethanol.

MACKOR [10] established that the zero-point of charge of AgI lies at a much lower concentration of I^- in acetone than in water (see also Ch. IV).
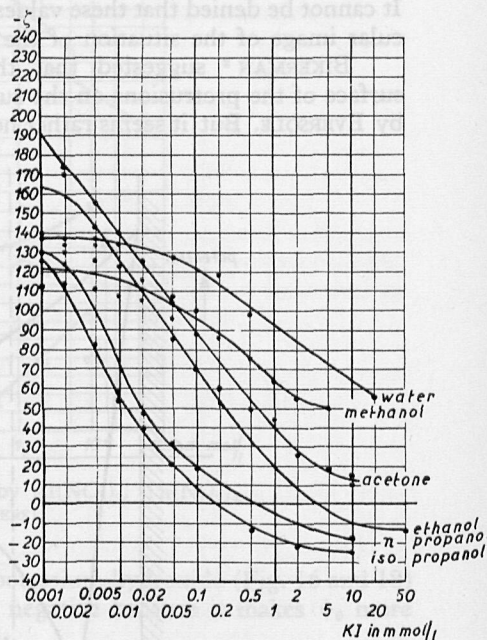
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[1] See for instance H. FREUNDLICH and G. ETTISCH, Z. physik. Chem., 116 (1925) 401.

[2] G. GOUY, Ann. phys., (9) 7 (1917) 179, already introduced the concept of "triple layer" in his theory of the positive branch of the electrocapillary curve.

[3] cf. H. R. KRUYT and S. A. TROELSTRA, Kolloid Beihefte, 54 (1943) 262.

[4] A. COEHN and V. RAYDT, Ann. Physik, 30 (1909) 777; See also M. VON SMOLUCHOWSKI, Graetz Handbuch der Elektrizität und des Magnetismus II, Leipzig 1914, p. 403.

[5] F. FAIRBROTHER and M. J. BALKIN, J. Chem. Soc., 53 (1931) 389, 1564.

[6] A. STRICKLER and J. H. MATHEWS, J. Am. Chem. Soc., 44 (1922) 1647.

[7] J. PERRIN, J. chim. phys., 2 (1904) 607; 3 (1905) 50.

[8] M. DE SMET, and J. DELFOSSE, Mededeel. Koninkl. Vlaam. Acad. Wetenschap. Belg. Klasse Wetenschap., 4 (1942) no. 10.

[9] E. J. W. VERWEY, Rec. trav. chim., 60 (1941) 625.

[10] E. L. MACKOR, Rec. trav. chim. 70 (1951) 747

b. 3. Silver halides

Silver halides have been investigated extensively with electrophoresis methods. Moreover with the silver halides the zero-point of charge, and therewith an absolute value for the surface potential ψ_0 could be determined analytically [1]. A remarkable parallelism between ζ and ψ_3 could be established, insofar as the zeros of ψ_3 and ζ coincide and ζ is of the same order, though somewhat smaller than the ψ_0-potential[2], cf. Fig. 23.
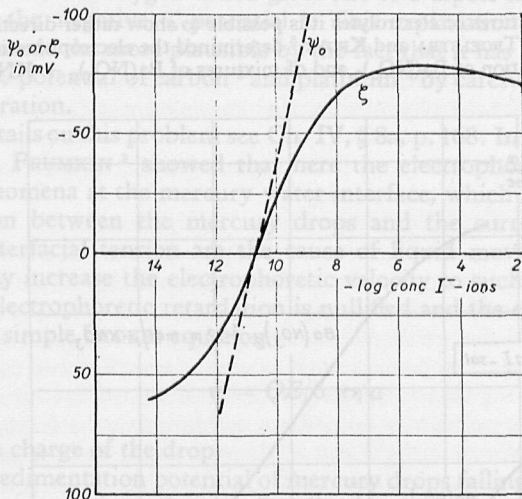

Fig. 23. ψ_0 - and ζ-potential of AgI against the logarithm of the I-concentration in the solution phase. ψ_3 is calculated according to

$$\psi_3 = \frac{RT}{F} \ln \frac{C_{I^-}}{10^{-10 \cdot 6}}$$

ζ is estimated from electrophoresis according to the equation

$$\zeta = \frac{4\pi \eta \, v}{\varepsilon}$$

The difference between ψ_0 and ζ has been discussed above (Figs. 20, 21). The zero-points of ζ and ψ_3 for the three silver halides are [3]

AgCl	$C_{Ag} = 10^{-4}$	$C_{Cl} = 10^{-5 \cdot 7}$
AgBr	$C_{Ag} = 10^{-5 \cdot 4}$	$C_{Br} = 10^{-6 \cdot 9}$
AgI	$C_{Ag} = 10^{-5 \cdot 5}$	$C_{I} = 10^{-10 \cdot 6}$

[1] E. J. W. VERWEY and H. R. KRUYT, Z. physik. Chem., A 167 (1933) 149; A. BASINSKI, Rec. trav, chim., 60 (1941) 267; I. M. KOLTHOFF and J. J. LINGANE, J. Am. Chem. Soc., 58 (1936) 1531; J. A. W. VAN LAAR, unpublished. cf. Ch. IV, § 6a, p. 161.

[2] S. A. TROELSTRA and H. R. KRUYT, Kolloid-Z., 101 (1942) 182.

[3] E. J. W. VERWEY and H. R. KRUYT, l.c.; A. BASINSKI, l.c.; G. H. JONKER, Thesis, Utrecht 1943. p. 32; E. LANGE and P. W. CRANE, Z. physik. Chem., A 141 (1929) 225; J. A. W. VAN LAAR, unpublished.

An effect, hitherto unexplained, was found first by JULIEN [1] on silver bromide and later by VERWEY [2] on the oxides of titanium and zirconium and by BUCHANAN and HEYMANN [3] on BaSO$_4$. In all cases the zero-point of ζ depended upon the degree of division of the wall material. Coarse crystals seemed to have a more negative character than fine ones. In the case of AgBr fine crystals (~ 50 mμ) were positive for Ag$^+$ concentrations above 10^{-6}, but a large crystal could not be charged positively even by 0.01 N Ag$^+$. The same phenomenon has been observed by JONKER [4] during the ageing of fresh AgBr sols where the zero-point is shifted to higher concentrations of Ag$^+$.

In electrophoresis in mixtures of electrolytes it is possible to show rather directly the influence of the time-of-relaxation effect. TROELSTRA and KRUYT [5] determined the electrophoretic velocity of silver iodide sol particles, with addition of Ba(NO$_3$)$_2$ and of mixtures of Ba(NO$_3$)$_2$ + KNO$_3$. In small con-
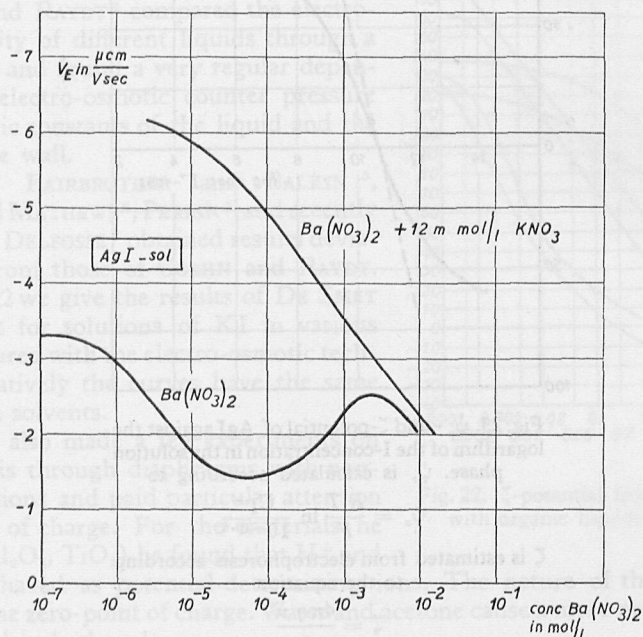

Fig. 24. Suppression of the time-of-relaxation effect by 12 m mol/1 KNO$_3$.

centrations of Ba(NO$_3$)$_2$ the electrophoretic velocity without KNO$_3$ is considerably smaller than with KNO$_3$. This may be explained by a suppression of the relaxation effect by KNO$_3$ in a concentration not sufficient to lower the ζ-potential considerably. In large concentrations of Ba(NO$_3$)$_2$ this electrolyte itself removes the relaxation effect so that further addition of KNO$_3$ remains without effect. See Fig. 24.

[1] P. F. J. A. JULIEN, Thesis, Utrecht 1933.

[2] E. J. W. VERWEY, Rec. trav. chim., 60 (1941) 625.

[3] A. S. BUCHANAN and E. HEYMANN, Nature, 161 (1948) 648, 691; J. Colloid Sci., 4 (1949) 137, 151, 157; See also R. RUYSSEN and R. LOOS, Nature, 162 (1948) 741.

[4] G. H. JONKER, Thesis, Utrecht, 1943, p. 30.

[5] S. A. TROELSTRA and H. R. KRUYT, Kolloid-Z., 101 (1942) 186, 187.

b. 4. *Metals*

ζ-potentials of *metals* have been investigated mainly by electrophoresis. As a consequence of the conductivity of metals electro-osmosis and streaming potential, although not altogether excluded, give rise to very complicated results [1].

Generally metals are negative with respect to water. An influence of the electromotive series cannot be recognized. Probably all metals (except mercury, see below) are covered by a layer of chemically adsorbed oxygen. The electrons of the metal-oxygen bond are displaced to the oxygen which gives rise to a dipole layer which may be seen as the cause of the negative ζ-potential [2]. This explanation of the influence of the oxygen layer is made the more plausible by the fact that it has been possible to reverse the sign of the ζ-potential of carbon [3] and platinum [4] by carefully excluding all oxygen during the preparation.

For more details on this problem see Ch. IV, § 8a, p. 168. In a remarkable investigation on mercury FRUMKIN [5] showed that here the electrophoresis is complicated by polarisation phenomena at the mercury-water interface, which results in differences of interfacial tension between the mercury drops and the surrounding liquid. These differences in interfacial tension are the cause of liquid movements in the mercury drops, which may increase the electrophoretic velocity to such an extent, that practically the whole electrophoretic retardation is nullified and the electrophoresis is nearly described by the simple STOKES equation

$$u = QE/6\,\pi\eta\,a$$

in which Q is the charge of the drop.

Also in the sedimentation potential of mercury drops falling in water, the easy flow of the liquid mercury gives rise to complications that have been investigated by FRUMKIN [6] and his school.

b. 5. *Oils and gases*

Oil and *paraffin* also generally show a ζ-potential in which the oil is negative. The influence of electrolytes is very much the same as for all other materials. As to the structure and the origin of these double layers, *cf.* however Chapter IV, § 7, p. 166 where the double layer at the interface of two liquids and at the interface liquid-air has been treated.

Even a completely inert and unsolid material as *air* may show electrokinetic pheno-

[1] *cf.* G. QUINCKE, *Pogg. Ann. Physik.*, 107 (1859) 1; 110 (1860) 38; H. R. KRUYT and J. OOSTERMAN, *Kolloid Beihefte*, 48 (1938) 377.

[2] J. H. DE BOER and E. J. W. VERWEY, *Rec. trav. chim.*, 55 (1936) 675.

[3] H. R. KRUYT and G. S. DE KADT, *Kolloidchem. Beihefte*, 32 (1931) 249.

[4] N. BACH and N. BALASCHOWA, *Acta Physicochim. U.R.S.S.* 3 (1935) 79; *Nature*, 137 (1936) 617.

[5] A. FRUMKIN, *J. Colloid Sci.*, 1 (1946) 227; I. A. BAGOTSKAYA, *J. Phys. Chem. U.S.S.R.*, 23 (1949) 1231; *Chem. Abstracts*, 44 (1950) 1306.

[6] A. FRUMKIN and V. LEVICH, *J. Phys. Chem. U.S.S.R.*, 21 (1947) 953; *Chem. Abstracts*, 42 (1948) 3244; A. FRUMKIN and I. A. BAGOTSKAYER, *J. Phys. & Colloid Chem.*, 52 (1948) 1.

mena. Air bubbles in water show electrophoresis. HERMANS [1] was able to measure the electro-osmosis at an air-water interface.

ζ-potentials and electrokinetic movements of *proteins* (and other hydrophilic colloids) and *association colloids* (*e.g.*, soaps) are treated extensively in Vol. II, chapters VII, IX, XI and XIV.

§ 10. TECHNICAL APPLICATIONS
OF ELECTROKINETIC PHENOMENA

QUINCKE was probably the first to think of technical applications of electrokinetics, when he proposed to use the phenomena of streaming potentials as a source of electric energy [2].

Although this proposal has never been put into practice electro-osmosis and electrophoresis have technical applications today.

Several patents of Graf SCHWERIN [3] exist on the removal of water from porous substances by electro-osmosis. The wet mass is placed between the electrodes, and the water is driven to one of the electrodes (mostly the cathode) where it drips off.

Electrophoresis has been used to apply a thin layer of small particles to a conducting carrier. If the particles are negatively charged, the conducting carrier is made the anode and the particles are deposited on it as a very compact and regular layer whose thickness can be easily regulated (it is proportional to the number of coulombs passed).

This electrodeposition may be carried out in organic media (ethanol, acetone, etc.), the advantage being absence of gassing at the electrodes even at relatively high currents and a low conductance of the liquid [4].

The particles may have colloidal dimensions [5], but even if they are larger (up to 10 or 20 μ) the process works quite satisfactory [6].

For more detailed theoretical considerations on electrophoretic deposition see [7].

The main fields of application of this "electrodeposition" are the preparation of insulated heater coils and of activated cathodes (a metal covered with a thin layer of oxides of the alkaline earths) for radio tubes and the preparation of rubber objects from latex. In the last-named case a metal form is used as an anode in a latex to which filling substances and vulcanizers have been added in finely divided form. In the deposit the different components are intimately mixed to a degree scarcely possible by mechanical methodes. After vulcanizing, the quality of rubber objects prepared in this way is very good [8].

[1] J. J. HERMANS, *Rec. trav. chim.*, 60 (1941) 747.

[2] G. QUINCKE, *Pogg. Ann. Physik*, 107 (1859) 1; 113 (1861) 513.

[3] D.R.P. nrs. 124509, 124510, 128085, 131932, 150069, 179086.

[4] J. H. DE BOER, H. C. HAMAKER and E. J. W. VERWEY, *Rec. trav. chim.*, 58 (1939) 662.

[5] E. PATAI and Z. TOMASCHEK, *Kolloid-Z.*, 74 (1936) 253; 75 (1936) 80.

[6] E. J. W. VERWEY and H. C. HAMAKER, *Trans. Faraday Soc.*, 36 (1940) 180; H. C. HAMAKER, *ibidem*, pg. 279.

[7] E. J. W. VERWEY and J. TH. G. OVERBEEK, *Theory of the stability of lyophobic colloids*, Amsterdam 1948, p. 178; C. G. A. HILL, P. E. LOVERING, and A. L. G. REES, *Trans. Faraday Soc.*, 43 (1947) 407.

[8] S. E. SCHEPPARD and L. W. EBERLIN, *Ind. Eng. Chem.*, 17 (1925) 711; P. KLEIN and A. SZEGVARI, Brit. Pat., 245 177, 246 532, 253 069.

§ 11. ABNORMAL OSMOSIS

A phenomenon that without a doubt is connected with electro-osmosis is the abnormal osmosis, known already to GRAHAM, but especially investigated by LOEB [1]. When two solutions of different concentrations are separated by a semi-permeable membrane, the normal osmotic movement is a transport of the solvent from the more dilute to the more concentrated phase. In many cases however, if the membrane is not rigorously impermeable to the solute a transport of liquid in the opposite direction is observed.

This transport may be explained as an electro-osmotic flow of the liquid through the pores of the membrane under the influence of the potential difference (diffusion potential) between the two liquid phases. That this explanation hits the nail on the head was demonstrated by LOEB, who showed, that, for a given membrane, the influence of electrolytes on abnormal osmosis and on electro-osmosis was similar if not identical.

§ 12. ON SURFACE CONDUCTANCE

In the preceding sections surface conductance has been repeatedly mentioned, but so far no detailed conception of this phenomenon has been found necessary. For all the applications it was sufficient to know the value of the extra conductivity along the interface but the mechanism of surface conductance was of no importance. In this section surface conductance will be examined for its own sake.

Experimental values of the surface conductivity have been mainly determined for the interface glass-solution of electrolyte in water. Unfortunately the results of different authors differ greatly from each other, partly as a consequence of the differences in the composition of the glass and the treatment before the measurements but probably also through inadequate experiments. In Table 3 values found by various authors are collected whereas Table 4 gives the values of the surface conductivity for a concentration of $5 \cdot 10^{-4}$ N KCl, KNO_3 or HCl. It is seen that there exist differences of a factor 100 between the different authors.

It is interesting now to compare the values of Tables 3 and 4 with the predictions of theory on the surface conductivity. Two different contributions to surface conductance have to be expected.

Firstly the double layer contains more ions than the bulk of the liquid. These excess ions cause one part of the surface conductivity by their motion in the electric field. Moreover the electro-osmotic movement, being fundamentally a displacement of the free charge of the double layer is another cause of surface conductance. This electro-osmotic contribution can only be observed in a d.c. field. If a.c. of sufficiently high frequence is used for measuring surface conductance, the electro-osmosis does not develop and only the first contribution will be found.

Roughly speaking it can be expected, that the first part of the surface conductivity is proportional to the mobility of the ions (explaining the large surface conductivity for HCl and HNO_3), and the second part to the charge of the double layer.

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[1] J. LOEB, *J. Gen. Physiol.*, 1 (1919) 717; 2 (1920) 173, 255, 387, 563, 577, 659, 673. *cf.* also F. A. H. SCHREINEMAKERS, *Proc. Acad. Sci. Amsterdam*, 27 and follow. vols.; *J. Gen. Physiol.*, 11 (1928) 701; 12 (1929) 555.

TABLE 3

VALUES OF THE SURFACE CONDUCTIVITY AS FOUND BY VARIOUS AUTHORS

Author	Sort of glass	Electrolyte	Normality	Surface conductivity in $10^{-9} \, \Omega^{-1}$
McBain, Peaker and King [1]	Pyrex (polished)	KCl	0.001 0.01 0.1	43 93 30—130 ?
McBain and Foster [2]	Pyrex	KCl	0.001 0.01 0.1	100 608 2640
Urban, Feldman, White [3]	Pyrex	KCl	0.0005 0.001 0.01	4.3 8.2 35
Fricke and Curtis [4]	Pyrex	KCl	10^{-4} 10^{-3} $8 \cdot 10^{-3}$	0.4 0.6 1.8
Rutgers, Moorkens, Verlende [5]	Jena 16$^{\mathrm{III}}$	KCl	0 10^{-5} 10^{-4} $2 \cdot 10^{-4}$ $5 \cdot 10^{-4}$	3 6 21 41 95
		HCl	10^{-5} 10^{-4} $2 \cdot 10^{-4}$	5 47 92
Wijga [6]	Pyrex	KNO$_3$	0 10^{-5} 10^{-4} $2 \cdot 10^{-4}$	0.7 1 4 5
		HNO$_3$	10^{-5} 10^{-4} $2 \cdot 10^{-4}$ 10^{-3}	3 20 31 88
Rutgers and De Smet [7]	Jena 16$^{\mathrm{III}}$	KCl	0 10^{-5} 10^{-4}	0.6 0.6 0.6

[1] J. W. McBain, C. R. Peaker, A. M. King, *J. Am. Chem. Soc.*, 51 (1929) 3294; *cf.* also J. W. Mc. Bain and C. R. Peaker, *J. Phys. Chem.*, 34 (1930)1033.

[2] J. W. McBain and J. F. Foster, *J. Phys. Chem.*, 39 (1935) 331.

[3] F. Urban, S. Feldman, and H. L White, *J. Phys. Chem.*, 39 (1935) 605; H. L. White, B. Monaghan, and F. Urban, *J. Phys. Chem.*, 40 (1936) 207.

[4] H. Fricke, and H. J. Curtis, *J. Phys. Chem.*, 40 (1936) 715.

[5] A. J. Rutgers, Ed. Verlende, and Ma. Moorkens, *Proc. Acad. Sci. Amsterdam*, 41 (1938) 763; A. J. Rutgers, *Trans. Faraday Soc.*, 36 (1940) 69.

[6] P. W. O. Wijga, *Thesis*, Utrecht 1946.

[7] A. J. Rutgers and M. De Smet, *Trans. Faraday Soc.*, 43 (1947) 102.

TABLE 4

SURFACE CONDUCTIVITY OF GLASS IN CONTACT WITH SOLUTIONS OF $0.0005\ N$ IN $10^{-9}\ \Omega^{-1}$

	McBain	White	Fricke	Rutgers (1938)	Rutgers (1947) [1]	Wijga
KCl	95	2.2—4.3	⌣ 1	95	⌣ 1	8
KNO₃						
HCl				225 (extrapol.)		
HNO₃						50

This theory of surface conductivity has been worked out by several authors [2] leading for univalent ions to the expression

$$\lambda\,\text{surf.} = \sqrt{\frac{\varepsilon\,RT}{2\,\pi\,F^2}c}\ \left[(e^{\frac{e\,\zeta}{2\,kT}}-1)\,(L_+ + \frac{\varepsilon\,RT}{2\,\pi\,\eta}) + (e^{-\frac{e\,\zeta}{2\,kT}}-1)\,(L_- + \frac{\varepsilon\,RT}{2\,\pi\eta})\right]$$

with the labels: over the first exponential term "electro osmosis"; over the second exponential term "electro osmosis"; under the first L_+ term "ionic mobility"; under the second L_- term "ionic mobility" (36)

To this value (36) URBAN, WHITE and STASSNER added a contribution caused by the mobility of the ions of the STERN layer, where normal mobility and a normal contribution to electro-osmosis of the STERN ions is supposed. Although this supposition does not *a priori* sound very probable, it cannot be denied that its results are rather well in accord with the experiments of WHITE and collaborators. However, this agreement does not prove very much in view of the wide divergencies shown in Tables 3 and 4.

Theoretical values of the surface conductance to be compared with those of Table 4 are given in Table 5.

TABLE 5

CALCULATED SURFACE CONDUCTANCE FOR SOLUTIONS OF $5 \cdot 10^{-4}\ N$

ζ is supposed to be 120 mV,
adsorption potential of STERN ions 70 mV,
total potential of the double layer 180 mV.

	Gouy layer alone	Gouy + Stern
surf. cond. KCl ($\approx$ KNO₃)	$1.4 \cdot 10^{-9}$	$4 \cdot 10^{-9}$
HCl ($\approx$ HNO₃)	$5 \cdot 10^{-9}$	⌣ $18 \cdot 10^{-9}$

[1] Recently RUTGERS by a new and efficient technique could confirm and improve the low values of the surface conductivity which are found to be only slightly dependent upon concentration (private communication). The same order of magnitude has been reported by I. I. ZHUKOV and D. A. FRIDRIKHSBERG, *Kolloid. Zhur.*, 11 (1949) 163-171, cited from *Chem. Abstracts*, 43 (1949) 7290.

[2] J. J. BIKERMAN, *Kolloid-Z.*, 72 (1935) 100; F. URBAN, H. L. WHITE, and E. A. STASSNER, *J. Phys. Chem.*, 39 (1935) 311.

If the theoretical values of Table 5 are compared with the experimental values of Table 4 it is striking that most authors find values much higher than the theoretical ones [1].

It appears as if an extra adsorption or at least an extra conductance exists, which is completely independent of the electrokinetic phenomena. One might think here of conductance through the swollen surface layer of the glass, although it is by no means clear how a quantitative explanation can be based upon this supposition.

It seems very important to gather more material on surface conductance preferably also on better defined surfaces than glass. In the field of surface conductance the disadvantages of glass seem to be more important than the advantages whereas for electrokinetic measurements the reverse was the case (*cf.* page 226).

§ 13. ELECTRICAL CONDUCTIVITY OF COLLOIDAL SOLUTIONS

Although electrical conductance and dielectric constants of colloids do not strictly belong to the electrokinetic phenomena they are so closely connected with them, especially with the electrophoresis, that it seems unavoidable to discuss them here.

The electrical conductance of a colloidal solution can be considered to be built up from contributions of the colloidal particles and the ions present in the solution. In a more schematic way the conductivity can be split up into a contribution of the sol particles and their counter ions (micellar conductivity) and a contribution of the rest of the liquid (intermicellar conductivity). This second method is mostly used in the practice of conductance measurements of colloids, but it should be realised that it is less exact than the first one. In the first place it is rather arbitrary to denote a certain part of the positive ions (the particles are supposed to be negatively charged) as counter ions and the rest of them as belonging to the intermicellar liquid. Moreover it neglects all interaction between the sol particles and the intermicellar ions, which is often not allowed.

Although it may be that the interpretation of conductivities of colloids cannot always be as precise as we should wish, in principle we know exactly how the interpretation should be given. In conductivity we see reflected the number, specific charge and mobility of the colloidal particles and the ions constituting the sol. Moreover we find in it the influence of the interaction of these components by electrophoretic and by time-of-relaxation effects. In some cases effects of association or dissociation may play a rôle too.

So it is not to be wondered at, that there are many applications of the conductivity of colloids, the number of which is certainly open to expansion. Several of these applications have contributed to our knowledge of the structure of the double layer.

To begin with an estimate will be made of the contribution to the conductivity of sol particles under very simplified conditions. We assume a concentration of 1% by volume of sol particles with a diameter $(2a)$ of 100Å and a ζ-potential of 100 mV in an electrolyte solution in which $\varkappa = 10^5$.

The charge of each particle may be put equal to

$$Q = a \, \varepsilon \, \zeta \, (1 + \varkappa \, a)$$

---

[1] See the remark on p. 237, that the latest results of RUTGERS also point to a *low* experimental value of the surface conductance.

The electrophoretic velocity neglecting the time-of-relaxation effect is

$$v = \frac{\varepsilon \, \zeta}{6 \, \pi \, \eta} = \frac{Q}{6 \, \pi \, \eta \, a \, (1 + \varkappa a)}$$

The number of particles per cm³ is

$$N = \frac{0.01}{\dfrac{4 \, \pi}{3} \, a^3}$$

and their contribution to the specific conductance

$$\Lambda \, \text{coll} = NQv = \frac{0.01}{\dfrac{4 \, \pi}{3} \, a^3} \, a \, \varepsilon \, \zeta \, (1 + \varkappa a) \, \frac{\varepsilon \, \zeta}{6 \, \pi \, \eta} = \frac{0.01 \, \varepsilon^2 \, \zeta^2 \, (1 + \varkappa a)}{8 \, \pi^2 \, a^2 \, \eta}$$

After the introduction of practical units the specific conductivity expressed in $\Omega^{-1} \, \text{cm}^{-1}$ is

$$\Lambda \, \text{coll} \approx 4 \cdot 10^{-5} \, \Omega^{-1} \, \text{cm}^{-1}$$

As the conductivity of a solution of an electrolyte with $\varkappa = 10^5$ is of the order of $10^{-6} \, \Omega^{-1} \, \text{cm}^{-1}$ the contribution of the colloidal particles should be easily measurable. Nevertheless the case mentioned above is a rather favourable one (small particles, high concentration), so it may be understood that there have frequently been discussions about the reality of the conductivity of colloidal particles. See for instance a discussion between PAULI [1] and WINTGEN [2] on the conductivity of gold sol where WINTGEN proved that the conductivity was less than $10^{-7} \, \Omega^{-1} \, \text{cm}^{-1}$ and PAULI, who found a much larger value, was probably misled by the ionic contribution to the conductivity. (See also Ch. IV, § 8 b, p. 172).

One of the most useful applications of the conductivity of colloids is found in the conductivity titration of ionic constituents of the sol. The method was introduced and fruitfully applied by PAULI [3], but has later on been used by many others. An example which is especially illuminating in this respect is the conductivity titration of the H^+- ions forming the counter ions of a negatively charged AgI-sol.

A titration curve [4] is represented in Fig. 25. The titration curve has the same character as that of a completely dissociated acid (dotted curve), with one exception: the slope of the neutralizing branch is much smaller than that of the hydroiodic acid.
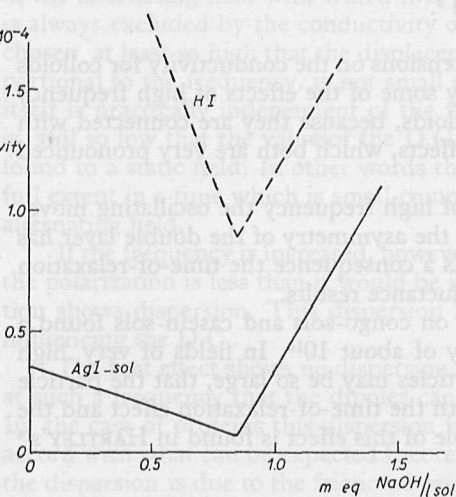
Fig. 25. Conductivity titration of a completely dialysed AgI sol (H^+ as counter ions) with NaOH. Dotted curve: titration of HI of the same equivalent concentration as the AgI sol with NaOH.

[1] W. PAULI and L. FUCHS, *Kolloidchem. Beihefte*, 21 (1925) 195, 412.
[2] R. WINTGEN and W. HACKER, *Kolloid-Z.*, 61 (1932) 335.
[3] W. PAULI and E. VALKO, *Electrochemie der Kolloide*, Vienna 1929, p. 289.
[4] H. DE BRUYN and J. TH. G. OVERBEEK, *Kolloid-Z.*, 84 (1938) 186.

It is as if the whole neutralizing branch has been depressed by a factor 4 or 5. This cannot be explained by a partial dissociation of the counter ions. In that case the neutralizing branch would be curved. So the small slope must be due to a strong hindrance of the counter ions by electrophoretic and by time-of-relaxation effects. In this way the titration of counter ions not only offers a quantitative determination of their number and therewith of the charge of the colloid particles, but gives also indications about their localization and fixation in the double layer.

Van Os [1] used the difference in mobility between the ions in the double layer and the ions in the "intermicellar liquid" to measure the exchange of ions by conductometry. He "titrated" an $(AgI)I^-H^+$-sol with barium nitrate. The H^+-ions were exchanged against the added barium ions. This caused an increase of the mobility of H^+-ions and a decrease for the Ba^{++}-ions. Because of the much larger mobility of the H^+-ions the total effect of exchange is an increase in conductivity which could be measured, and which served as a means of evaluating the exchange quantitatively.

Incidentally the results of these experiments could be completely described by the theory of the diffuse double layer. Cf. Chapter IV, § 9a, p. 177.

The specific conductivity and the transport number as a function of the concentration have been especially useful for the elucidation of the structure of association colloids such as soaps. For details the reader is refered to Chapter XIV of volume II, where these matters are treated in more detail [2].

The influence of high-frequency and high tensions on the conductivity for colloids is just the same as for normal electrolytes. Only some of the effects of high frequency or high tensions are more pronounced with colloids, because they are connected with the electrophoretic and the time-of-relaxation effects, which both are very pronounced with particles of colloidal dimensions.

If the conductivity is measured in a field of high frequency the oscillating movement of the particles may become so rapid that the asymmetry of the double layer has not enough time to develop to its full extent. As a consequence the time-of-relaxation effect loses part of its efficacy and a rise of conductance results.

So Schmidt and Erkkila [3] experimenting on congo-sols and casein-sols found a rise in conductance of 6–30% for a frequency of about 10^{10}. In fields of very high tensions (100,000 V/cm) the velocity of the particles may be so large, that the particle is drawn out of its ionic atmosphere, so that both the time-of-relaxation effect and the electrophoretic retardation disappear. An example of this effect is found in Hartley's [4] work on paraffin-chain salts.

§ 14.   THE DIELECTRIC CONSTANT OF COLLOIDS

a.   Theoretical considerations

The dielectric constant of colloidal solutions is different from that of the pure dispersion medium. This difference can be ascribed to four different effects.

The *first* effect is a simple volume effect. Part of the dispersion medium is replaced

[1] G. A. J. Van Os, *Thesis*, Utrecht 1943.
[2] *cf.* also G. S. Hartley, *Aqueous solutions of paraffin-chain salts*, Coll. Hermann, Paris 1936.
[3] G. Schmidt and A. V. Erkkila, *Z. Electrochem.*, 42 (1936) 737, 781; *cf.* also H. J. Curtis and H. Fricke, *Phys. Rev.*, (2) 48 (1931) 775.
[4] J. Malsch and G. S. Hartley, *Z. physik. Chem.*, A 170 (1934) 321.

by the sol particles which as a rule have a much lower dielectric constant than the medium, so that the total dielectric constant (D.C.) is lowered by this effect.

Secondly the sol particles may possess a permanent dipole moment. This dipole moment is oriented by the electric field thereby enhancing the polarization and the D.C. For hydrophobic colloids this effect is mostly of small importance as these particles do not contain a permanent dipole moment. But for some hydrophilic colloids especially for proteins the existence of a permanent moment is probable. In these cases a considerable increase of the D. C. may be found.

Thirdly the electric double layer exerts an influence on the D.C.. As has been explained in the sections on electrophoresis and conductivity the electrical double layer is distorted by the electric field. The centres of gravity of the positive and negative charges no longer coincide. The particle acquires a dipole moment directed oppositely to the field and enhancing the dielectric constant. This effect is of importance with all colloids (whether hydrophobic or hydrophilic) provided with a double layer.

Finally the hydration or solvation may have an influence on the dielectric constant. The water of hydration is under the influence of strong adsorption forces and one may expect that its polarizability may be increased or decreased; although a decrease, owing to the fixation of the molecules, seems more probable resulting in a decrease of the D.C..

It should be kept in mind, that generally the D.C. is a function of the frequency of the alternating field with which it is measured. Measuring with a really static field is always excluded by the conductivity of the sols. The frequency of the field must be chosen at least so high that the displacement current, related to the D.C. which is proportional to the frequency, is not small compared with the conduction current, which itself is practically independent of the frequency. In favourable cases this frequency is still so low that the value of the D.C. is not different from the value that would be found in a static field. In other words the polarization of the colloid can develop to its full extent in a time which is small compared with the duration of one pulsation of the alternating field.

If the frequency is increased, however, this last condition may no longer be fulfilled; the polarization is less than it would be in a static field of the same strength. The solution shows dispersion. This dispersion has a different character for the four factors influencing the D.C..

The first effect shows no dispersion. The dispersion of the second effect is situated at such a frequency that the dipoles can no longer follow the alternations of the field. In the case of proteins this dispersion frequency is found at about 10^6 cycles/sec [1], in accord with what can be expected theoretically [2] if the protein particles are spheres and the dispersion is due to the frictional resistance of the sphere in the viscous medium.

The third effect will show dispersion at a frequency where the asymmetry of the double layer is no longer developed. This means the frequency at which the conductivity shows an increase. Simultaneous measurements of the two effects are, alas, lacking although the dispersion of the D.C. as well as that of the conductivity has been demonstrated.

Whether the influence of the hydration on the D.C. is subject to dispersion is questionable. Moreover as will be shown in the following it is not sure that the effect itself has yet been measured.

[1] J. ERRERA, *J. chim. phys.*, 29 (1932) 577.
[2] J. TH. G. OVERBEEK, *Natuurw. Tijdschr.*, 18 (1936) 55.

The quantitative side of the theory of the D.C. of colloids has not been developed to any great extent. The situation is the most favourable for the simple mixing effect. As we are concerned with heterogeneous systems, we may apply the theory of WIENER [1], who proposed a very general method for calculating the D.C. of heterogeneous mixtures. For a small concentration (δ by volume) of spherical paricles having a D.C. ε_1, embedded in a liquid of D.C. ε_0, the D.C. ε is given by

$$\varepsilon = \varepsilon_0 \left(1 - 3\, \frac{\varepsilon_0 - \varepsilon_1}{2\,\varepsilon_0 + \varepsilon_1}\, \delta\right) \tag{37}$$

It is seen that the relative change of the D.C. falls between

$$\frac{1}{\varepsilon}\frac{d\varepsilon}{d\delta} = -1.5 \qquad \text{for } \varepsilon_1 \ll \varepsilon_0$$

and

$$\frac{1}{\varepsilon}\frac{d\varepsilon}{d\delta} = +3 \qquad \text{for } \varepsilon_1 \gg \varepsilon_0$$

For elongated particles the effect may be larger.

The influence of dipoles on the D.C. is probably described most satisfactorliy by the theory of ONSAGER [2], according to which the D.C. of a mixture as treated above, having moreover a permanent dipole moment μ in each spherical particle, is given by ($\varepsilon_1 \ll \varepsilon_0$)

$$\varepsilon = \varepsilon_0 \left(1 - \frac{3}{2}\,\delta\right) + \frac{(\varepsilon_1 + 2)^2\,\mu^2}{4\,kTa^3}\, \delta \tag{38}$$

The relaxation time (reciprocal of the dispersion frequency) is given by

$$\tau = \frac{8\,\pi^2\,\eta\,a^3}{kT} \tag{39}$$

where a is the radius of the particles.

A quantitative relation between the D.C. and the double layer (third effect) is very difficult to give because the increase of the D.C. rests completely upon the time-of-relaxation effect, and we know already from the electrophoresis how difficult calculations of this effect are.

More or less elaborate theories have been given by BIKERMAN [3], HERMANS [4] and OVERBEEK [5]. Probably the best way to get a quick estimation of the magnitude of this effect is to start from the notion of surface conductance. A particle, surrounded by a layer conducting much better than the dispersion medium, behaves as if it were a conducting particle.

According to WIENER's theory, the D.C. of a suspension of conducting particles can be easily calculated, as conducting particles may be symbolized by particles with

[1] O. WIENER, *Abhandl. math. phys. Klasse sächs Akad. Wiss.* Leipzig, 32 (1912) 507; *cf.* D. A. G. BRUGGEMAN, *Ann. Physik*, (5) 24 (1935) 636.
[2] L. ONSAGER, *J. Am. Chem. Soc.*, 58 (1936) 1486.
[3] J. J. BIKERMAN, *J. chim. phys.*, 32 (1935) 285.
[4] J. J. HERMANS, *Phil. Mag.*, (7) 26 (1938) 650.
[5] J. TH. G. OVERBEEK, *Kolloid Beihefte*, 54 (1943) 287.

an infinitely large D.C. ($\varepsilon_1 = \infty$). As radius of the conducting particles we chose the radius of the particles proper increased with the thickness of the double layer ($1/\varkappa$). So a relative increase of the D.C. may be expected which is of the order of

$$\frac{1}{\varepsilon} \frac{d\varepsilon}{d\delta} \sim 3 \left(1 + \frac{1}{\varkappa \, a} \right)^3 \tag{40}$$

The dispersion frequency of this effect may be expected to be the same as that of the electrolyte solution in which the particle is embedded. This dispersion frequency is given by the theory of strong electrolytes as [1]

$$\nu = \frac{\varkappa^2 \, kT}{\rho} \tag{41}$$

ρ is the average friction constant of the ions in the double layer.

b. Experimental evidence

Perhaps the most simple example has been measured by PIEKARA [2]. He investigated the D.C. of emulsions of paraffin in water, by which eq. (37) was rather well confirmed. Small but systematic deviations from (37) suggested a small influence of the double layer.

Somewhat more complicated were the experiments by KRUYT and KUNST [3] on various hydrophobic sols (silver halides, arsenic sulphide). They found an increase of the D.C. of the order expected from eq. (40) with $\varkappa \, a \sim 0.5$ or 1.0. The dispersion frequency was also in accord with eq. (41). So in these experiments the double layer probably played the most important rôle. Nevertheless the influence of added electrolytes was not clear in all respects. More experiments and a more refined theory are desired here.

Analogous effects were found by FRICKE [4] on the D.C. of suspensions of different oxides and hydroxides.

Very interesting results were obtained by ERRERA [5] for the D.C. of sols of vanadium pentoxide. Aged sols containing very long particles showed an excessively high D.C., for instance a sol containing 1% V_2O_5 had a D.C. of over 400! An investigation [6] of the double refraction in alternating fields of these sols made it probable that the effect is due to polarization of the double layer, the D.C. rising to such exceptionally high values because the particles of V_2O_5 are oriented with their long axis in the direction of the field, thereby greatly facilitating the polarization.

The influence of permanent dipoles has been supposed to be present in ERRERA's [7] experiments on proteins.

By application of eq. (38) the dipole moments of a molecule of protein was found

[1] J. TH. G. OVERBEEK, *l.c.*

[2] A. PIEKARA, *Kolloid-Z.*, 58 (1932) 283 and 59 (1932) 12.

[3] H. R. KRUYT and H. KUNST, *Kolloid-Z.*, 91 (1940) 1.

[4] H. FRICKE and L. HAVESTADT, *Z. anorg. Chem.*, 188 (1930) 357; 196 (1931) 120.
H. FRICKE, *Kolloid-Z.*, 56 (1931) 166.

[5] J. ERRERA, *J. phys. radium*, (6) 3 (1922) 401; 4 (1923) 225; 9 (1928) 307; *Kolloid-Z.*, 31 (1922) 59; 32 (1923) 157, 373.

[6] J. ERRERA, J. TH. G. OVERBEEK, and H. SACK, *J. chim. phys.*, 32 (1935) 681.

[7] J. ERRERA, *J. chim. phys.*, 29 (1932) 577.

to be of the order of 500 D, a value in itself not improbable. But it seems very difficult to separate experimentally the influence of permanent dipoles from that of the double layer also known to exist.

Finally we shall devote a few lines to the effect of hydration. DENEKAMP and KRUYT[1] found an increase of the D.C. of gelatin and agar-agar at a frequency of 10^6 sec^{-1}.

They explained this increase by the hydration of these substances. But as the criteria of hydration are open to much doubt, and other influences (double-layer, permanent dipole) also give rise to an increase of the D.C., the interpretation of KRUYT and DENEKAMP seems debatable.

At very high frequencies both the double layer and the permanent dipoles should lose their influence on the D.C., the only remaining effects being the mixing effect and the influence of hydration. Experiments by KRUYT and OVERBEEK[2] showed that for high frequencies $(3.5 \cdot 10^8)$ the D.C. of gelatin, albumin, and other hydrophilic colloids could be completely explained by the mixing effect (eq. 37), no influence of the hydration being detectable.

[1] P. J. DENEKAMP and H. R. KRUYT, *Kolloid-Z.*, 81 (1937) 62.
[2] H. R. KRUYT and J. TH. G. OVERBEEK, *Kolloid-Z.*, 81 (1937) 257.