

# QUANTITATIVE INTERPRETATION OF THE ELECTROPHORETIC VELOCITY OF COLLOIDS

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## I. Introduction

When an electric field is applied to a colloidal solution, in many cases, the colloidal particles are observed to migrate to one of the electrodes. This phenomenon, described in 1861 by Quincke (56), is termed cataphoresis or, better and more generally, electrophoresis.

In the development of colloid science, electrophoretic experiments have played a very great part indeed. There probably is not a single other

method of investigation that has been so widely applied in pure as well as in applied research of colloids. This may be explained by the fact that a number of techniques for the determination of the electrophoretic mobility are available, which ask only for a comparatively simple experimental setup. Another factor in favor of electrophoresis certainly has been the attractive and simple interpretation of Helmholtz (33) and Smoluchowski (61,62), permitting calculation of the *zeta potential* from the electrophoretic mobility.

The classical investigations of Hardy (32), Powis (55), and Burton (15) introduced the concept that the stability of hydrophobic colloids is closely related to the zeta potential as calculated from electrophoresis. A specified minimal zeta potential (the *critical potential*) was found to be necessary to keep the hydrophobic suspension stable. This concept has been very widely used, and, although in more recent concepts of the stability of colloids (71,73,74) the zeta potential has a less predominant position, electrophoresis still remains an important source of information about hydrophobic colloids.

With hydrophilic colloids the relation between stability and electrophoresis is much less prominent because many hydrophilic colloids may remain in colloidal solution even when their electrophoretic mobility is reduced to zero. Nevertheless, in this domain also electrophoresis retains its significance for the determination of the isoelectric point and of the charge of the particles outside the isoelectric point. In mixtures of hydrophilic colloids, again, stability is related to electrophoresis. Complex coagulation—that is, a phase separation in which a mixture of hydrophilic colloids is precipitated in the form of a very concentrated liquid—occurs only if the two colloids are oppositely charged and if the charge of each is sufficiently high (14). This charge can be, and is actually in most cases, evaluated from electrophoresis.

Although the usual methods of determining electrophoretic mobility of hydrophobic colloids are not directly applicable to hydrophilic systems, because the scattering of light by the latter is much slighter than that of hydrophobic colloids, the technique of measuring electrophoresis of hydrophilic colloids adsorbed on small inert particles as coal, quartz, oil droplets, etc. (2) is widely applicable and easy to manage.

Moreover, the method of Tiselius (65,66), which uses the difference in optical density between a colloidal solution and its dialyzate, and thereby adapts the moving boundary technique to hydrophilic colloids, enjoys a continually increasing interest especially in the field of proteins. It has been very frequently used for the determination of purity of protein prepa-

rations, and for the quantitative analysis and separation of protein mixtures. In the application of this method, however, the interpretation of the electrophoretic mobility in terms of the charge or potential of the particles has somewhat fallen into the background. Not so much because the evaluation of the electrophoretic mobility would be difficult in this method (it may be so in dilute solutions), but perhaps because in many applications of the Tiselius technique (quantitative separations, proof of purity), the relation between electrophoretic mobility and charge of the particles is inessential.

In every textbook on colloid science and in many books on general physical chemistry, electrophoresis is treated. Moreover, two excellent monographs of Abramson on the subject exist. The first of these (1), however, dates back to 1934; the second (4), published in 1942, deals especially with proteins.

In the following pages we shall direct our attention particularly to the quantitative interpretation of the electrophoretic mobility. Such a survey seems not to be wholly superfluous as, even in recent times, there exist many controversial opinions on the subject and, although by far not all the problems presented here have been completely solved, the situation seems to be cleared sufficiently to justify a review of this type.

## II. Classical Concepts of Electrophoretic Velocity

In 1879 Helmholtz (33) presented a theory of electrokinetic phenomena, one of which is electrophoresis, and made clear that the electrophoretic velocity is proportional to the zeta potential and not, as one might imagine upon first thought, to the charge of the colloidal particle.

### 1. Equation of Helmholtz-Smoluchowski

The derivation of Helmholtz has been improved and extended by Smoluchowski without, however, essentially altering the final result. Smoluchowski's analysis was in the first instance directed upon electro-osmosis and he derived his electrophoresis equation by simply remarking that electrophoresis is the reverse phenomenon from electro-osmosis, so that, for the relative motion of liquid and solid the same equation applies to both phenomena. As we are concerned here especially with electrophoresis, we will give Smoluchowski's derivation in an abridged form and in direct application to electrophoresis.

In a solution of electrolyte, a suspended particle assumes as a rule a certain charge, a compensating charge of the opposite sign and equal magnitude staying in the solution in the neighborhood of the charged particle.

The extension of this compensating charge in the solution is of the same order as the thickness,  $1/\kappa$ , of the Debye-Hückel ionic atmosphere:

$$\frac{1}{\kappa} = \left( \frac{\epsilon k T}{4\pi e^2 \sum n_i z_i^2} \right)^{1/2} \quad (1)$$

in which  $\epsilon$  is the dielectric constant,  $e$  the elementary charge,  $z_i$  the valency,  $n_i$  the number of ions of species  $i$  per cubic centimeter,  $k$  Boltzmann's constant, and  $T$  the absolute temperature.

By application of Poisson's equation:

$$\Delta\psi = -4\pi\rho/\epsilon \quad (2)$$

in which  $\Delta$  is the operator of Laplace,  $\psi$  the potential, and  $\rho$  the charge density in the double layer and Boltzmann's theorem, the distribution of charge and potential around the particle, can be derived, but since in Smoluchowski's derivation, an explicit expression for the distribution of charge is superfluous, we will postpone this point until Section 3.

With Smoluchowski we assumed a rigid particle of *arbitrary form* embedded in a solution. The surface of the particle has a potential  $\zeta$  with respect to the liquid far from the particle. If one wishes to assume that a layer of liquid adheres so firmly to the particle that it cannot be set into motion either by an applied electric field, or by a motion of the liquid, this layer shall be considered as forming part of the particle, the potential  $\zeta$  being found now at the boundary of the fixed and the free liquid.

The existence of such a fixed layer of liquid was postulated by Smoluchowski (61) in order to explain the difference between the total potential in the double layer ( $\epsilon$ -potential) obeying the equation of Nernst, and the  $\zeta$  potential. The difference between these two potentials is located in the adhering liquid layer and perhaps in the solid phase too.

Lamb (41), contrary to Helmholtz and Smoluchowski, assumed the possibility of a slip between solid and liquid in the electrokinetic movements. The experimental arguments for such a slip are, however, far from convincing and, as far as our knowledge of the boundary phenomena goes at present, slip does not seem to occur.

Bikerman (7) recently discussed the theory of the adhering liquid layer and tried to explain the difference between  $\epsilon$  and  $\zeta$  potentials by the surface roughness of solids. A layer of liquid, without being in the true sense fixed to the solid, would be kept from moving with the bulk of the liquid by the protruding parts of the surface. It should be kept in mind, however, that in Smoluchowski's analysis the form of the particles is immaterial. Roughness of the surface could only influence the electrokinetic phenomena if the roughness is on a scale smaller than the thickness of the double layer, thereby invalidating Smoluchowski's next assumption on the dimensions of the particle.

The *dimensions* of the particle are so large that the radius of curvature at any point of the surface is large compared to the extension of the double layer.

The particle is considered to be *nonconducting*, whereas the *electric conductance* of the liquid, its *dielectric constant*, and *viscosity* are assumed to have the same value in the double layer as in the bulk of the liquid.

All three assumptions are debatable. The electric conductance in the surface layer may be higher than the bulk conductance (see Sect. III.2).

The viscosity might well be influenced by the presence of the solid surface. This effect, however, is at least formally accounted for by the assumption of the adhering water layer (in which the viscosity would be infinitely high).

The *dielectric constant* in the double layer might be changed by a loss of mobility of the liquid molecules adsorbed to the surface and by a change in composition of the liquid near the surface. As long as there is no direct experimental evidence of this change in dielectric constant, which there is not at present, it seems not useful to introduce a change in dielectric constant as an extra complication in the theory.

The *electric field* applied to produce electrophoresis may be distorted by the presence of the particle but is otherwise additively superimposed upon the field of the double layer.

As the radius of curvature of the particle surface is large, the potential gradient of the double layer is to a good approximation perpendicular to the surface. The applied electric field has only a component parallel to the surface, because the particle is nonconducting. If we call this field strength  $\mathbf{E}$ , it is easy to demonstrate that just outside the double layer the velocity of the liquid with respect to the particle is directed along  $\mathbf{E}$  (parallel to the surface) and has the value:

$$\mathbf{v} = -\frac{\epsilon\zeta}{4\pi\eta} \mathbf{E} \quad (3)$$

where  $\eta$  is the viscosity of the liquid.

The derivation of equation (3) can be given along the following lines. The charge density,  $\rho$ , in the double layer is given by Poisson's equation (2), which may be written:

$$\rho = -\frac{\epsilon}{4\pi} \frac{d^2\psi}{dn^2}$$

in which  $n$  is the outward normal on the surface. A volume element of the liquid is subjected to two equal forces of opposite directions, one due to the applied electric field working on the charge in the double layer, the other due to viscous friction.

As in the neighborhood of the surface, the motion of the liquid is parallel to the surface, the force exerted by viscous friction on a thin layer of liquid,  $dn$ , is equal to the difference in the forces transmitted on both sides of the thin layer, that is equal to:

$$\left( \eta \frac{d\mathbf{v}}{dn} \right)_{n=n} - \left( \eta \frac{d\mathbf{v}}{dn} \right)_{n=n+dn} = -\eta \frac{d^2\mathbf{v}}{dn^2} dn$$

The force exerted by the external field on the net charge present in this layer is given by  $\rho\mathbf{E} dn$ . Equating the two forces we get the equation:

$$\rho \mathbf{E} = -\frac{\epsilon}{4\pi} \frac{d^2\psi}{dn^2} \mathbf{E} = -\eta \frac{d^2\mathbf{v}}{dn^2}$$

Integrating once we find:

$$\frac{\epsilon}{4\pi} \frac{d\psi}{dn} \mathbf{E} = \eta \frac{d\mathbf{v}}{dn} + c_1$$

$$c_1 = 0 \text{ because for } n \rightarrow \infty, (d\psi/dn) = (d\mathbf{v}/dn) = 0$$

The second integration gives:

$$\frac{\epsilon}{4\pi} (\psi_\infty - \zeta) \mathbf{E} = \eta (\mathbf{v}_\infty - \mathbf{v}_0)$$

With  $\psi_\infty = 0$  and  $\mathbf{v}_0 = 0$ , this is equivalent to equation (3)

Under the influence of the applied electric field, the particle moves with a certain constant speed,  $u$ , in the direction of the field. With respect to a system of coordinates fixed to the particle, the liquid at a great distance from the particle moves with velocity  $-u$ . In the immediate neighborhood of the particle, the velocity of the liquid is given by equation (3), and in intermediate regions the velocity has to satisfy the condition of incompressibility, *viz.*:

$$\operatorname{div} \mathbf{v} = 0 \quad (4)$$

The solution of equation (4) and therewith the value of  $u$  is easily found by remarking that the applied electric field obeys an equation analogous to equation (4):

$$\operatorname{div} \mathbf{E} = 0 \quad (5)$$

and that the boundary conditions at the surface of the particle for  $\mathbf{v}$  and  $\mathbf{E}$  are proportional to each other according to equation (3). Consequently the velocity of the liquid is everywhere parallel and proportional to the electric field  $\mathbf{E}$  and especially at a large distance from the particle:

$$v = -\frac{\epsilon\zeta}{4\pi\eta} E$$

where  $E$  is the value of the applied field at some point far from the particle. Returning to a resting system of coordinates, the electrophoretic velocity  $u$  of the particle with respect to this system is given by:

$$u = \frac{\epsilon\zeta}{4\pi\eta} E \quad (6)$$

completely independent of the form and dimensions of the particle, if large enough.

With regard to the uncertainty in the value of  $\epsilon$  (see above), there have been proposals by Bull and Gortner (12) and Guggenheim (31), among others, to characterize the electrokinetic phenomena by the product of  $\epsilon$  and  $\zeta$ —being the electric moment of the double layer. Guggenheim even made a formal proposal to introduce the quantity  $\epsilon\zeta/12\pi$  and to call the unit of this quantity the *Helmholtz*. Although these proposals have a certain advantage in that they allow the double layer to be characterized unhampered by uncertainties in the dielectric constant, it should not be forgotten that we turn to electrokinetic experiments for information on the potential or the charge of the surface. To that end we must make some assumption (more or less well founded) on the value of  $\epsilon$  in the double layer.

## 2. Hückel Equation

In Smoluchowski's theory, the motion of the particle is governed by three different types of forces, although they have not been explicitly introduced into the calculation. The equation:

$$\frac{\epsilon}{4\pi} \frac{d\psi}{dn} \mathbf{E} = \eta \frac{d\mathbf{v}}{dn}$$

occurring in the derivation of Smoluchowski's equation, when applied to  $n = 0$ , is equivalent to:

$$-\sigma \mathbf{E} = \eta \left( \frac{d\mathbf{v}}{dn} \right)_{n=0}$$

in which  $\sigma$  is the charge density on the surface. This means that the electrical force on the surface charge is just counterbalanced by a viscous friction. This viscous friction can be regarded as consisting of two components.

(1) The viscous friction that would also be present if the liquid surrounding the particle would contain no charges.

(2) The force that would be exerted on the particle by that component of the motion of the liquid which is caused exclusively by the action of the applied field on the charges in the liquid part of the double layer. This force is called the "electrophoretic retardation." It is always retarding because the charge in the liquid is the opposite of that on the particle. These same forces are treated in the theory of conductance of strong electrolytes (20,50); Debye and Hückel (21) also applied to colloidal particles the method of calculation used in the theory of strong electrolytes. They confirmed Smoluchowski's equation (6) except for the factor  $1/4\pi$ , which should only have this value for a cylindrical particle migrating with its axis parallel to the field, whereas for other forms the factor should have another value. For a spherical particle Hückel (36) derived a factor  $1/6\pi$ .

Since Debye and Hückel stated that they used the same assumptions

of Smoluchowski, but did not show where the analysis of the latter was in error, there was a contradiction (remaining unsolved for several years) until Henry (34), in a renewed analysis of the whole problem, reconciled the two contradictory points of view.

### 3. Henry Solution of the Contradiction between Smoluchowski and Hückel Theories

The difference between the concepts of Smoluchowski and Debye and Hückel is to be found in the geometry of the applied electric field. Whereas Smoluchowski considers the particle as an insulator and takes the deformation of the applied field by the particle explicitly into account, Debye and Hückel simply assume that the value and the direction of the electric field have the same value throughout the whole system. The conception of Debye and Hückel is quite justified in the case of electrolytic solutions, because there the extension of the double layer is so much larger than the dimensions of the ions that the deformation of the field, which is only felt in the immediate neighborhood of the ions, is practically without influence upon the electrophoretic retardation.

In colloidal systems, however, which of the two concepts must be applied depends wholly upon the ratio of the extension of the double layer and the dimensions of the particles. If the particle is relatively large, the deformation of the lines of force has to be taken into account, which results in a smaller value of the electrophoretic retarding force. Hence Smoluchowski's value for the electrophoresis is larger than Hückel's.

Henry (34) worked out an electrophoresis equation for any ratio between the thickness of the double layer and the dimensions of the particle.

It is impossible to solve this problem with the same generality used by Smoluchowski; it is necessary to restrict the analysis to certain specified forms of the particle. Henry's calculations are restricted to spherical particles and cylinders with their axis parallel to, or perpendicular to, the direction of the applied field.

For the motion of the liquid Henry uses the same assumption as Smoluchowski and Debye and Hückel, *viz.*, the equations of Navier and Stokes, with a constant viscosity, incompressibility of the liquid, and a relative velocity zero at the spherical (or cylindrical) surface, where the potential of the double layer has the value  $\zeta$ . Henry, too, assumes that the outwardly applied field, although deformed by the presence of the particle, and the field of the double layer are simply additive.

Without any further approximation he thus derives the following

equation (7) for the electrophoretic mobility of a spherical isolating particle of radius  $a$ .

$$u = \frac{\epsilon E}{4\pi\eta} \left[ \zeta + 5a^5 \int_{\infty}^a \frac{\psi}{r^6} dr - 2a^3 \int_{\infty}^a \frac{\psi}{r^4} dr \right] \quad (7)$$

In order to work out the integrals in expression (7) it is necessary to introduce explicitly the dependence of potential  $\psi$  on distance  $r$ , measured from the center of the sphere. So apart from Poisson's equation (2), which has been used in the derivation of (7), it is necessary to introduce Boltzmann's theorem to establish a relation between the charge density,  $\rho$ , and the potential,  $\psi$ :

$$\rho = n_+ z_+ e \exp(-z_+ e\psi/kT) - n_- z_- e \exp(+z_- e\psi/kT) \quad (8)$$

where  $n_+$  and  $n_-$  are the concentrations,  $z_+$  and  $z_-$  the valencies of the positive and negative ions present in the solution. It is well known that an explicit solution of the combination of equations (2) and (8) can be found only when the exponents in (8) are so low that the exponentials may be developed and only the first term of the development is used, leading to:

$$\rho = -\frac{e^2}{kT} (n_+ z_+^2 + n_- z_-^2) \psi \quad (9)$$

When this approximation is used:

$$\psi(r) = \zeta a \frac{e^{\kappa(a-r)}}{r} \quad (10)$$

Inserting equation (10) into (7), relation (11) is found for the velocity of a spherical isolating particle:

$$u = \frac{\epsilon \zeta E}{6\pi\eta} \left[ 1 + \frac{\kappa^2 a^2}{16} - \frac{5\kappa^3 a^3}{48} - \frac{\kappa^4 a^4}{96} + \frac{\kappa^5 a^5}{96} - \left( \frac{\kappa^4 a^4}{8} - \frac{\kappa^5 a^5}{96} \right) e^{\kappa a} \int_{\infty}^{\kappa a} \frac{e^{-t}}{t} dt \right] \quad (11)$$

in which  $\kappa a$  gives the ratio between the extension of the double layer ( $(1/\kappa)$ , see Eq. 1) and the radius of the sphere,  $a$ .

In Figure 1 the equation of Henry is represented graphically. It will be clear that the deformation of the applied field is strongly dependent upon the electric conductance of the particle. Henry showed that this deformation and its influence upon the electrophoretic velocity is determined by the ratio  $\mu$  of the electrical conductivities of the particle and the surrounding liquid. His results for three typical cases,  $\mu = 0$ ,  $\mu = 1$ , and  $\mu = \infty$ , are given in Figure 1.

For cylindrical particles with their axis parallel to the field, the electrophoretic velocity is given by Smoluchowski's equation (proportionality factor  $1/4\pi$ ), independent of the thickness of the double layer or the conductivity of the particles.

For cylinders placed transverse to the field, Henry has given an electrophoresis equation analogous to equation (7), but he has only worked out

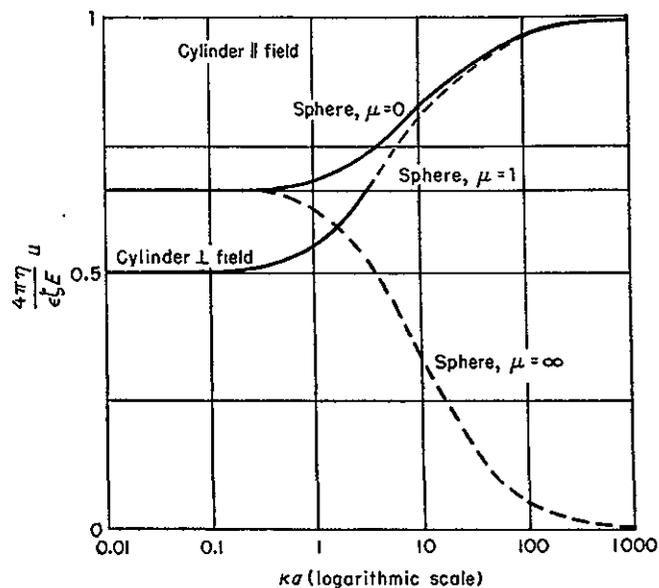


Fig. 1. Factor of proportionality between electrophoretic velocity  $u$  and zeta potential according to the theory of Henry (34).

the solution for the extreme cases that  $\kappa b = 0$  or  $\kappa b = \infty$  ( $b$  is the radius of the cylinder), finding for insulating particles a proportionality factor  $1/8\pi$  when the double layer is very extended and  $1/4\pi$  for a very thin double layer. When the cylinder is conducting the electrophoretic velocity in the case of a very thin double layer is zero, just as in the case of a conducting sphere.

Gorin (26) extended Henry's calculations on cylinders and determined the proportionality factor for intermediate values of  $\kappa b$ . His results are reproduced in Table I and Figure 1.

In applications to cylindrical particles, cylinders oriented randomly are often involved. Gorin (4, p. 127) determined an average mobility factor for random orientation by applying the relation:

$$\frac{3}{u_{\text{random}}} = \frac{2}{u_{\perp}} + \frac{1}{u_{\parallel}} \quad (12)$$

The reasons given for averaging the reciprocal values of the mobility rather than the mobility itself are not very convincing. Gorin defends this procedure by mentioning that, in the averaging, stress should be placed upon the distortion of the external field rather than on the mobility.

TABLE I  
Electrophoretic Mobility of Infinitely Long Cylindrical Particles (26)

$\kappa b$	$(4\pi\eta/\epsilon\zeta E)u$	
	Cylinder $\perp$ to field	Cylinder in random orientation
0	0.50	0.60
0.4	0.518	0.616
1.0	0.544	0.639
1.4	0.582	0.676
2.0	0.615	0.705
2.4	0.631	0.719
3.0	0.656	0.741
$\infty$	1	1

For particle forms other than cylinders, spheres, and flat plates no calculations have been made. Neither does there exist a theory of the electrophoresis of a randomly kinked long-chain molecule—of which colloids like gum arabic, pectic acid, and polyacrylic acid are interesting examples.

#### 4. Influence of Conductivity of Particles

In experiments on the electrophoretic displacement of a cylindrical silver wire in a solution of silver nitrate where polarization had been carefully excluded, Henry (34) could confirm the fact predicted by the theory that the electrophoretic velocity is zero for conducting cylinders, which are large in comparison to the thickness of the double layer.

It remains questionable, however, whether for true colloidal suspensions the case  $\mu = \infty$  is ever realized even for metallic particles, because the passing of an electric current through the particles necessarily entails a polarization of the surface, which may easily be large enough to stop completely any further current through the particle. Consequently the particle behaves as an insulator and the electrophoretic velocity should be calculated putting  $\mu = 0$ .

Mercury droplets, which certainly are large compared to the extensions

of the double layer, nevertheless show a normal electrophoretic mobility (13), which proves, as has already been remarked by Verwey (69), that they behave as insulators.

### 5. Electrophoresis of Liquid Droplets

Up to this point the considerations have been restricted to rigid particles. If this condition is dropped and one turns to the electrophoresis of the droplets of an emulsion, the state of the theory is rather disappointing. The friction experienced by a liquid droplet is certainly less than that of a

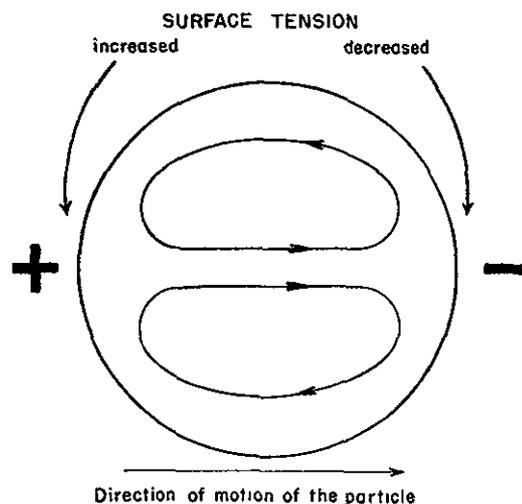


Fig. 2. Schematic representation of the motions in a drop of mercury placed in an electric field (23).

solid sphere of the same dimensions, because the drop of liquid can more or less adapt itself to the movements of the surrounding medium (10,60). On the other hand, the double layer at the interface of two liquids extends in both phases (70,72), and the part of it present in the droplet would be expected to play an active rôle in electrophoresis, giving rise to a circulating motion in the drop. The case has not, however, been analyzed theoretically.

A recent investigation of Frumkin (23) on the electrophoresis of mercury drops should be mentioned here too. Frumkin shows that in this case the mercury droplet is completely polarized by the applied field, so

that actually it behaves like an insulator. The polarization, however, alters the surface tension on the poles of the particle thereby generating motions of the mercury along the interface. If the mercury is positively charged (as is normally the case), the surface at the pole facing the positive electrode is negatively polarized, whereby its surface tension increases, whereas at the other pole it decreases. The motion of mercury generated by this difference in surface tension is schematically represented in Figure 2. It can be seen that this motion would support the motion of the particle to the negative electrode thus enhancing the electrophoretic velocity.

Frumkin has shown by experiments and theoretically that, especially when the surrounding medium is very viscous, the electrophoretic velocity may be increased enormously above the value calculated from Smoluchowski's equation by a factor of the order of  $10^4$  or  $10^5$ , so that in this special case the velocity is practically given by the simple equation of Stokes, where  $Q$  is the charge of the drop:

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

## III. Influence of Deformation of Double Layer upon Electrophoresis

### 1. Relaxation Effect

In the considerations of the two foregoing sections, an essential supposition was that the electric field due to the double layer and the externally applied field may be simply superimposed on each other. This is certainly not exactly the case, as the particle and the outer part of the double layer, having opposite signs of charge, move in opposite directions, by which means the original symmetry of the double layer is disturbed. By electric conduction and diffusion, the double layer tends to restore its symmetry but this restoration takes a certain time, the *time of relaxation*, and the outer part of the double layer lags somewhat behind the particle. This gives rise to an additional electric field, which is directed oppositely to the applied field, and retards the electrophoretic motion.

In the conductance of strong electrolytes, the influence of this *relaxation effect* is of the same order of magnitude as the retardation caused by the motion of the ions of the atmosphere, *electrophoretic retardation* (20,50). Hence, in order to arrive at a complete description of electrophoresis, it seems necessary to include this relaxation effect.

Several investigators have approached this problem. The first was Paine (54), who applied the equation of Debye and Hückel directly to colloidal particles. However, as in the theory of electrolytic conductance

no account is taken of the deformation of the applied field (see above), this theory is valid only for small values of  $\kappa a$  ( $\kappa a < 1/10$ ). It can be seen from Figure 3 that the field of interest of colloid science, *viz.*, particles of dimensions between 10 Å. and 1  $\mu$  and values of  $\kappa$  between  $10^5$  and  $10^{7.5}$  (concentrations of electrolyte in water from  $10^{-5}$  to 1  $N$ ) only coincides for a very small area with the region in which  $\kappa a < 1/10$ .

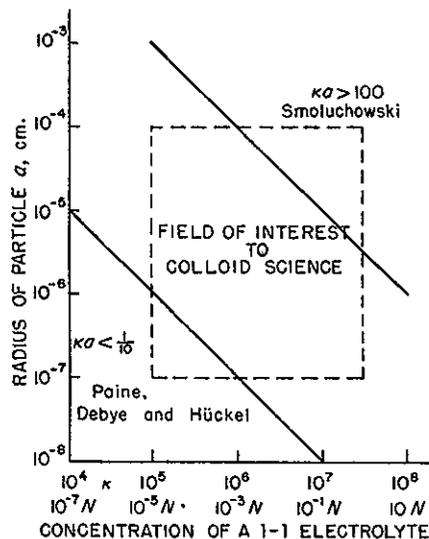


Fig. 3. Field of interest to colloid science compared to fields in which  $\kappa a$  is larger than 100 or is smaller than 0.1 (51, 53, 54).

On the other hand, it is possible to show that for large values of  $\kappa a$  ( $\kappa a > 100$ ), where  $a$  is one of the main dimensions of a particle of arbitrary form, the correction due to the relaxation effect is less than a few per cent. (In this region Henry's correction, too, is of the order of 3% or less.)

We repeat here the proof of this theorem given by Overbeek (51) in an abridged and somewhat simplified form.

The relaxation effect can be described as an extra field  $F$  (opposing the applied field  $E$ ), which is generated by the transport of charge along the particle. This transport of charge is effected by the applied field and by the electrophoretic motion itself, and it is counteracted by diffusion and conduction. When the double layer is thin, diffusion plays only a secondary role, so that in the stationary state of electrophoresis the conduction should just balance the two first-named effects.

The primary transport of charge by the applied field is proportional to the circum-

ference of the particle, the field strength  $E$ , and the charge density of the surface, which itself is proportional to  $\kappa\zeta$ . Consequently this transport can be expressed as a current  $i_I$ .

$$i_I \sim E\zeta\kappa a$$

The transport of charge by the electrophoresis itself is likewise proportional to the circumference of the particle, the charge density of the surface, and the velocity  $u$  of the particle, which itself is proportional to  $E$ . Therefore the second current is:

$$i_{II} \sim E\zeta\kappa a$$

The conduction current balancing these two currents  $i_I$  and  $i_{II}$  is not restricted to the surface of the particle but passes in the surrounding medium through a cross section of the order of  $a^2$  and is proportional to:

$$i_{III} \sim Fna^2$$

where  $n$  is the number of ions per cubic centimeter. As  $\kappa^2 \sim n$ :

$$i_{III} \sim F\kappa^2 a^2$$

Consequently, by putting  $i_{III} = i_I + i_{II}$  we find:

$$F\kappa^2 a^2 \sim E\zeta\kappa a$$

or:

$$F/E \sim \zeta/\kappa a$$

To take the relaxation effect into account, we must replace  $E$  in the equation of Smoluchowski by  $E - F$  and we find:

$$u = \frac{\epsilon\zeta}{4\pi\eta} (E - F) = \frac{\epsilon\zeta E}{4\pi\eta} \left\{ 1 - \frac{\text{const. } \zeta}{\kappa a} \right\} \quad (13)$$

which immediately shows that the correction for relaxation goes to zero when  $\kappa a$  becomes large enough. By a somewhat more accurate reasoning than the one given above, it is possible to obtain an idea about the magnitude of the constant in equation (13), which is of the order of  $e/kT$ . This means that the correction amounts to about 1% when  $\kappa a = 100$  and  $\zeta = 25$  mv.

The fact that for relatively large particles Smoluchowski's (or Henry's) equation retains its validity, even if account is taken of the relaxation correction, explains a very interesting series of observations summarized by Abramson (1). It was observed that the electrophoretic mobility of *microscopic* particles of widely divergent shapes and dimensions is exactly the same when the surface of the particles may be considered to be identical. In many cases the identity of the surfaces has been attained by covering the particles, which may have very different chemical properties (oil, graphite, iron oxide, quartz, asbestos, etc.) by a layer of protein. In the circumstances of these experiments, the thickness of the double layer (which varied between  $\sim 0.1 \mu$  (distilled water) and  $0.001 \mu$  (solutions)

was always small compared to the dimensions of the particles (which varied between 0.5 and several hundred microns). So it is in complete accord with the theoretical developments given above that all show the same electrophoretic mobility, which, incidentally, is the same as the electro-osmotic mobility. This, however, does not imply that the relaxation effect may also be neglected for smaller particles. It can be seen in Figure 3 that there still exists a large region of interest to colloid science (between  $\kappa a = 1/10$  and  $\kappa a = 100$ ) in which the influence of the relaxation effect may be expected to be more important.

In the existing literature there are relatively few papers on the relaxation effect of colloids. Only three deal with the case of large  $\kappa a$ . Of these, Mooney (48) and Bikerman (8,9) come to equations analogous to our equation (13), Mooney, however, without stating clearly how his equation has been derived and Bikerman only for a very special case, *viz.*, a long, but not infinitely long, cylinder parallel to the field. The third author, Hermans (35) treats the case of a spherical particle and arrives at a much larger relaxation effect than that given by equation (13). It seems that his derivations contain an omission, namely, the relative influence of the relaxation effect and the electrophoretic retardations, which makes his results of too large an order of magnitude (see also (52)). The work of Paine (54) for the case of very small values of  $\kappa a$  has already been mentioned.

Komagata (39) calculated the influence of the relaxation effect including any values of  $\kappa a$ . Although his basic work is sound, the calculations contain several mistakes, which make his results valueless.

Overbeek (52,53) has given a derivation of the relaxation effect for spherical particles valid for arbitrary values of  $\kappa a$ . Very recently Booth (11) in a short communication announced independent work on the same subject, which, in the main lines, seems to confirm Overbeek's analysis. As details of Booth's work are not yet available, a short description of Overbeek's method of approach and the most important of his results are given.

The calculations of electrophoretic mobility (including relaxation) for intermediate values of  $\kappa a$ , although in principle not more difficult than for the extreme cases of small or large  $\kappa a$ , are in practice very laborious and time consuming. This is, among other things, due to the fact that for intermediate and large values of  $\kappa a$  we may no longer consider the effects of relaxation and electrophoretic retardation separately, as we do for electrolytes (small  $\kappa a$ ). For larger values of  $\kappa a$ , it is essential to include in the calculations the mutual influence of the two effects. Moreover, it can be inferred from the considerations on the relaxation effect for very small and

very large  $\kappa a$  that the correction for the relaxation effect will be proportional to the square, and possibly higher powers, of the zeta potential. This implies that also in the distribution of the potential around the particle higher powers of zeta must be included.

In Overbeek's calculations the particle is assumed to be a rigid sphere with a surface potential  $\zeta$  and a charge  $ne$  spread out uniformly over the surface. (Booth used a more general assumption about the charge of the surface.) The particle is embedded in a solution of a  $(z_+ - z_-)$  valent electrolyte. It is surrounded by a diffuse double layer of the Gouy-Chapman type (18,29), which, however, is deformed by the electrophoresis.

The motion of the ions is governed by displacement in the electric field, by diffusion in concentration gradients, and by being dragged along by the movements of the liquid. During electrophoresis a stationary state is attained in which, relative to the moving particle, the concentration of each sort of ion remains constant. The particle is considered to acquire a constant velocity  $u$  in the direction of the applied field.

The equations for the stationary state are:

$$\operatorname{div} \left[ -\frac{n_+ z_+ e}{\rho_+} \operatorname{grad} \psi - \frac{kT}{\rho_+} \operatorname{grad} n_+ + n_+ \mathbf{v} \right] = 0 \quad (14)$$

$$\operatorname{div} \left[ +\frac{n_- z_- e}{\rho_-} \operatorname{grad} \psi - \frac{kT}{\rho_-} \operatorname{grad} n_- + n_- \mathbf{v} \right] = 0$$

where  $n_+$  and  $n_-$  represent the number of ions per cubic centimeter,  $\rho_+$  and  $\rho_-$  their friction constants, and  $\psi$  the electric potential due to the combined effects of double layer, applied field, and deformation by the relaxation effect.

By assuming a uniform motion for the central particle, its Brownian movement is neglected. This analysis is thus more in accord with the original Debye and Hückel theory (20) of conductance of strong electrolytes than with the later improved analysis of Onsager (50). In solutions of a single electrolyte, the correction of Onsager is essential because in the original version of the theory, which leaves the Brownian movement of the central ion out of account, the relaxation forces on the positive and negative ions are different, whereas, of course, the equality of action and reaction requires that the two forces are of equal magnitude. In a colloidal solution, however, the particles with their double layers are always embedded in a solution of electrolyte and, except in the cases of very concentrated and highly dialyzed sols, the total charge on the colloidal particles is only a very small fraction of the total charge of all the ions present in the solution.

Consequently the colloidal solution can be compared to a solution of electrolyte to which a small proportion of a second electrolyte has been added. Bennowitz, Wagner, and K uchler (6) have given an evaluation of the relaxation effects for such a mixture taking

Brownian motion into account. From their analysis one finds, neglecting the Brownian motion of the ion present in small quantity, an increase of the relaxation correction with a factor of the order:

$$1 + \rho_1/\rho_2$$

in which  $\rho_1$  and  $\rho_2$  are the frictional constants of the ions present in large and small quantity, respectively. As the diameter of a colloidal particle is at least 10 times and often 100 or more times as large as that of an ion, neglecting the Brownian motion in the case of colloids is completely justified.

The relations between charge density and potential in equation (14) are again given by Poisson's equation (2). Since the particle is considered to be an insulator, no discharge of either type of ions occurs at the surface of the particles. (For a consideration of a conducting particle see (52).)

The above considerations define the electric field and the ionic concentrations in the double layer, except for the value of the motion of liquid,  $v$ , in equation (14). The motion of the liquid can be completely described by the fundamental hydrodynamic equations:

$$\begin{aligned} \operatorname{div} v &= 0 \\ \eta \operatorname{rot} \operatorname{rot} v + \operatorname{grad} p + \rho \operatorname{grad} \psi &= 0 \end{aligned} \quad (15)$$

By a method of successive approximations it is possible to solve equations (14) and (15) and the resulting equation for the electrophoretic mobility is, including all terms up to  $\zeta^3$ .

$$\begin{aligned} u = \frac{\epsilon \zeta E}{6\pi\eta} \left[ f_1(\kappa a) - (z_- - z_+) \frac{e\zeta}{kT} f_2(\kappa a) + (z_+ z_-) \left( \frac{e\zeta}{kT} \right)^2 g_1(\kappa a) - \right. \\ \left. (z_+^2 - z_+ z_- + z_-^2) \left( \frac{e\zeta}{kT} \right)^2 g_2(\kappa a) + (z_- - z_+)^2 \left( \frac{e\zeta}{kT} \right)^2 g_3(\kappa a) - \right. \\ \left. \frac{z_+ \rho_+ + z_- \rho_-}{(z_+ + z_-) e} \cdot \frac{\epsilon kT}{6\pi\eta e} \cdot \left( \frac{e\zeta}{kT} \right)^2 f_4(\kappa a) \right] \quad (16) \end{aligned}$$

The functions  $f(\kappa a)$  and  $g(\kappa a)$  except  $g_3(\kappa a)$  have been calculated. For symmetrical electrolytes the electrophoretic equation can be simplified to:

$$u = \frac{\epsilon \zeta E}{6\pi\eta} \left[ f_1(\kappa a) - z^2 \left( \frac{e\zeta}{kT} \right)^2 f_3(\kappa a) - \frac{\rho_+ + \rho_-}{2e} \frac{\epsilon kT}{6\pi\eta e} \left( \frac{e\zeta}{kT} \right)^2 f_4(\kappa a) \right] \quad (17)$$

and for unsymmetrical electrolytes, neglecting all contributions proportional to  $\zeta^3$  except the last term, which is preponderant even over the  $\zeta^2$  terms for small values of  $\kappa a$ :

$$u = \frac{\epsilon \zeta E}{6\pi\eta} \left[ f_1(\kappa a) - (z_- - z_+) \frac{e\zeta}{kT} f_2(\kappa a) - \frac{z_+ \rho_+ + z_- \rho_-}{(z_+ + z_-) e} \frac{\epsilon kT}{6\pi\eta e} \left( \frac{e\zeta}{kT} \right)^2 f_4(\kappa a) \right] \quad (18)$$

Figure 4 and Table II show the values of the functions  $f(\kappa a)$ .  $f_1(\kappa a)$  has not been included in Figure 4 because it is identical with Henry's function  $f(\kappa a, \mu = 0)$ , which can be read from Figure 1. The broken line in Figure 4 shows the values of  $f_2$  and  $f_4$  as they follow from Debye and Hückel's theory of the conductivity of strong electrolytes.

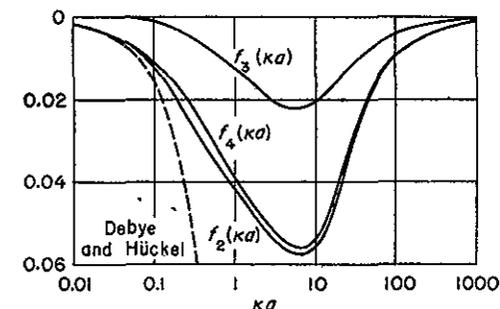


Fig. 4. Values of the functions  $f(\kappa a)$  for use in the electrophoresis equations (17) and (18).

TABLE II

Values of Correction Terms in Equations (17) and (18)

$\kappa a$	$f_1(\kappa a)$	$f_2(\kappa a)$	$f_3(\kappa a)$	$f_4(\kappa a)$
0.01	1.000006	0.0006	0.00009	0.0006
0.1	1.000545	0.0125	0.00090	0.0107
0.3	1.00398	0.0279	0.0044	0.0218
1	1.0267	0.0411	0.0116	0.0387
3	1.1009	0.053	0.020	0.051 <sub>6</sub>
5	1.160	0.057	0.022	0.054 <sub>6</sub>
10	1.239	0.05 <sub>6</sub>	0.021	0.05 <sub>6</sub>
20	1.34	0.04	0.014 <sub>6</sub>	0.04
50	1.424	0.0188	0.00796	0.0177
100	1.458	0.0102	0.00444	0.00992
1000	1.495	0.0011	0.0005	0.0011

To illustrate the total influence of the correction of Henry and the relaxation effect on the electrophoretic velocity, Figures 5 and 6 are given. Both have been drawn for an equivalent conductance of the positive and negative ions equal to  $70 \Omega^{-1} \text{ cm.}^2$  per gram equivalent (this value is not

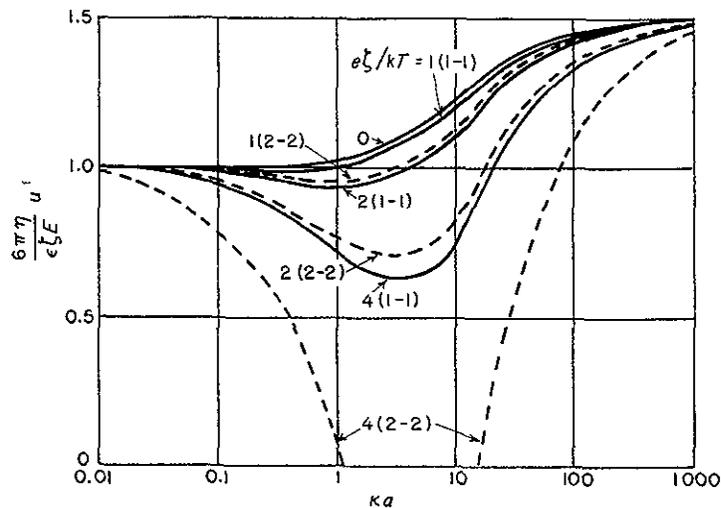


Fig. 5. Electrophoretic mobility in symmetrical electrolytes (Eq. 17). Values of  $e\zeta/kT$  are 1, 2, and 4 or  $\zeta$  about 25, 50, and 100 mv., respectively. The line marked 0 forms the limit for very small values of the zeta potential. Full lines for monovalent and broken lines for bivalent electrolytes.

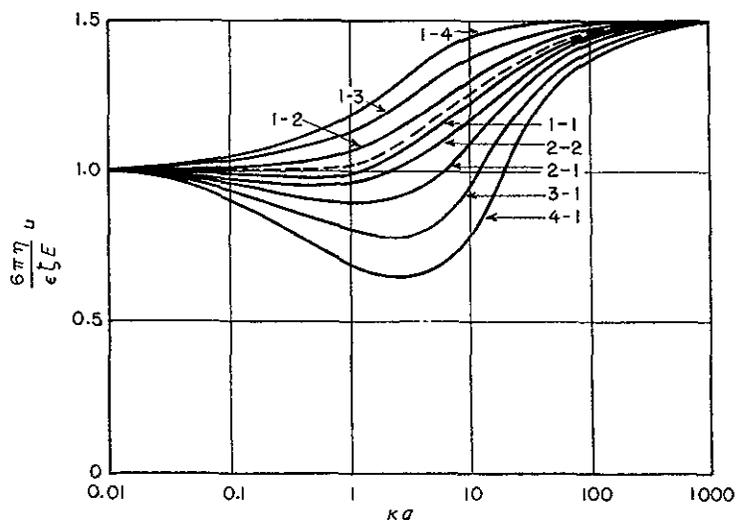


Fig. 6. Electrophoretic mobility in unsymmetrical electrolytes (Eq. 18). For all the curves  $e\zeta/kT$  values equal 2 or  $\zeta$  about 50 mv.

very critical), and a temperature of 25°C. Figure 5 represents equation (17) for symmetrical electrolytes; Figure 6 gives equation (18) for unsymmetrical electrolytes. In Figure 5,  $e\zeta/kT$  varies from very small values ( $e\zeta/kT \rightarrow 0$ ) to 4, which means that the zeta potential varies from 0 to about 100 mv. For the higher values of  $\zeta$  it would have been necessary to include more terms of the series; they should be seen only as a rough illustration of the trend of the electrophoretic velocity. In Figure 6,  $\zeta$  is fixed at 50 mv. ( $e\zeta/kT = 2$ ) but the type of electrolyte has been varied.

It is conspicuous that the correction for relaxation is largest for intermediate values of  $\kappa a$ , which are of the order of 5–10. Since the corrections are proportional to the second and higher powers of  $\zeta$ , they tend to reach zero for small values of  $\zeta$ . With increasing potentials and increasing valency of the ions, the corrections increase rapidly. But for monovalent electrolyte and zeta potentials smaller than 25 mv. the relaxation effect is small for any  $\kappa a$  and the corrections to Henry's equation never exceed 3%.

This small value of the relaxation effect justifies many an application of Henry's equation to proteins, for which the electrophoretic mobility often remains smaller than  $1 \mu \text{ cm. v.}^{-1} \text{ sec.}^{-1}$ , which is equivalent to a zeta potential smaller than 20 mv. at 25°C., or 35 mv. when the electrophoresis has been carried out at 0°.

Figure 6 shows the remarkable fact that, with unsymmetrical electrolytes, the relaxation effect may be accelerating instead of retarding if it is the ion bearing the same charge as the particle that is polyvalent.

## 2. Influence of Surface Conductance

It is to be expected that the double layer is a source of surface conductance and we should investigate in what respects surface conductance influences the electrophoretic mobility.

In 1903 Smoluchowski (62) pointed out that the net charge of the double layer results in a specific surface conductivity equal to (for small values of  $\zeta$ ):

$$\frac{1}{\eta d} \left( \frac{\epsilon \zeta}{4\pi} \right)^2$$

in which  $d$  is the thickness of the double layer. Moreover, the concentrations of ions in the double layer are different from those in the bulk of the liquid, and as the changes in concentrations for positive and negative ions are different, a second contribution to the surface conductance results. Both these effects are incorporated in the theory of relaxation and, therefore, no extra corrections are needed.

In several experiments, especially on glass-water interfaces (see Table III), however, surface conductivities have been measured which far exceed the values to be expected from the simple theory of the diffuse double layer. Just as, according to Henry's calculations, the mobility is decreased by a certain conductivity of the particle as a whole, an excessively large surface conductance would have the same effect, lowering the mobility of a spherical particle with a factor (11):

$$1 + \lambda_s/\lambda a$$

in which  $\lambda_s$  is the specific surface conductance and  $\lambda$  the bulk conductance of the liquid. However, as long as there are such wide divergencies in the experimental values as shown in Table III, any further discussion of this effect seems to be premature.

TABLE III

Specific Surface Conductivities (in  $10^{-9} \Omega^{-1}$ ) of Glass in Contact with Solutions of 0.0005 N Electrolytes

Reported by	KCl	KNO <sub>3</sub>	HCl	HNO <sub>3</sub>
McBain (45-47).....	95	—	—	—
White (68,75,76).....	2.2-4.3	—	—	—
Fricke (22).....	1	—	—	—
Rutgers (57,59).....	95	—	225	—
Wijga (77).....	—	8	—	50

Recently Booth (11a) and Henry (34a) independently discussed the influence of surface conductance on electrophoresis. They concluded that, especially with small particles, the electrophoretic velocity could be very much lower than that given by equation (6).

### 3. Summary of Conditions in Which Zeta Potential Can Be Evaluated from Electrophoresis

The practical consequence of the theoretical developments in this section is that in certain well-defined cases  $\zeta$  can be confidently evaluated from the electrophoretic mobility. They are:

(1) For any value of  $\kappa a$  if the  $\zeta$  potential is smaller than 25 mv. and the particle is spherical or nearly so. Application of Henry's equations is essential; the correction for relaxation can be calculated by the above theory or may be neglected if an inaccuracy of a few per cent is not essential.

(2) For large values of  $\kappa a$  and any value of  $\zeta$  irrespective of the form of the particle, by application of Smoluchowski's equation.

In both cases the particle should be an insulator or at least behave as such. There should be no excessive surface conductance. In analogy to the results obtained for spherical particles, it seems safe to assume that also for other forms of the particles (especially for cylinders for which the calculations of Henry and Gorin are available) the relaxation effect remains small in the two conditions mentioned above. In all other cases the quantitative evaluation of zeta potentials from electrophoresis has the element of great uncertainty.

### 4. Experimental Work

Experiments allowing a quantitative test of the theory are unfortunately very scarce. Even the simple equations of Smoluchowski and Henry have never been really tested, and even a convincing test of the theory of the relaxation effect does not exist.

One of the reasons is that it is very difficult to determine zeta potential in an independent way. De Bruyn (19) has indicated an interesting method of determining the zeta potential by potentiometry which, as far as order of magnitude is concerned, confirms the values by electrokinetic methods. But a closer comparison of the two principles is still lacking.

Other electrokinetic phenomena, especially electro-osmosis and streaming potential, may be used to determine  $\zeta$ , but then the identity of the surfaces in the two types of experiments is hard, if not impossible, to insure.

The most satisfying results are obtained by a comparison of electro-osmosis and electrophoresis of relatively large particles covered with a layer of protein to insure identity of the surfaces. These experiments give ample confirmation of the reliability of the factor of proportionality in Smoluchowski's equation, that is, for the identity of the electro-osmotic and electrophoretic velocity for large  $\kappa a$  (4). In many of the experiments of this type the electrophoretic velocity was rather low ( $< 1 \mu\text{cm. v.}^{-1} \text{sec.}^{-1}$ ), so that the relaxation effect would be expected to be small anyway.

Mooney (48) did some experiments on the electrophoresis of oil drops of different diameter in which a lowering of the electrophoretic velocity with decreasing radius of the particles was established. Qualitatively this is in accord with equations (13) and (16). Quantitatively the effects of Mooney seem to be larger than the theoretical predictions. His experiments, however, are not so exact that they form a serious test of the theory. Moreover, the fact that they have been performed with emulsions may have caused complications (see Sect. II.5.)

For very small particles of CuO, Fe<sub>2</sub>O<sub>3</sub>, and As<sub>2</sub>S<sub>3</sub> sols at very low elec-

trolyte concentrations ( $\kappa a < 1/10$ ), Paine found a linear dependence of the mobility from  $\kappa$ , which is in accord with the applicability of the theory of Debye and Hückel if the charge of the particles is assumed to be constant. The slope of the  $u$  versus  $\kappa$  line determines the value of the radius of the particles, which seemed to be of the right order of magnitude, but has not been determined independently.

In view, however, of the arguments given in the beginning of the next section (see also (73)), it is rather doubtful whether in this case the charge is really independent of  $\kappa$ , so that the arguments of Paine cannot be considered to be decisive.

Other experimental data will be treated at the end of Section IV.

Finally it may be mentioned that the maxima often found in electrophoretic mobility as a function of the concentration of the electrolyte may perhaps be explained as an increase of the relaxation effect on the low-concentration side of the maximum and a real decrease of  $\zeta$  at the other side. The fact that those maxima are usually found in colloids with relatively large particles, where the "pure sols" may have a value of  $\kappa a$  of the order of 1-10, corroborates this explanation. In principle the same explanation has already been given by Bikerman (8,9).

## IV. Electrophoretic Velocity and Charge of Particles

### 1. Charge and Potential

In the foregoing sections attention has been concentrated on the evaluation of the zeta potential. The charge of the particles necessary to generate this potential has been treated as a magnitude of only secondary importance. This point of view seems entirely justified in the case of hydrophobic suspensions, emulsions and the like because, in all probability, their surface potential is much more characteristic than the surface charge. Indeed, if the particle is considered to be in thermodynamic equilibrium with the surrounding liquid, its potential is completely determined by the distribution of certain ions, which are present in both phases (38,43). Consider, as an example, a particle of a silver halide in contact with its saturated solution, which may contain an excess of the silver or halide ions and, in addition, any amount of other electrolytes. Then for equilibrium the chemical potential  $\mu_{Ag^+}$  of the silver ions must have the same value in both phases. In the solid phase the chemical potential depends only upon the characteristic structure of the solid and upon its potential:

$$\mu_I = \mu_I^0 + e\psi_I$$

where the index I designates the silver halide phase. In the solution

$\mu_{II}$  depends on the potential of the liquid and moreover on the ionic activity:

$$\mu_{II} = \mu_{II}^0 + e\psi_{II} + kT \ln a_{Ag}$$

In equilibrium,  $\mu_I = \mu_{II}$ , or

$$e(\psi_I - \psi_{II}) = \mu_{II}^0 - \mu_I^0 + kT \ln a_{Ag} \quad (19)$$

which means, that if the activity of the silver ions in the solution (the potential-determining ions) is given (43), the potential difference between the two phases is fixed, whereas the charge density on the surface may still vary widely dependent on the thickness of the double layer.

On the other hand the situation changes completely if, instead of considering particles of hydrophobic sols, we turn our attention to the electrophoresis of large molecules like proteins. Here the whole concept of zeta potential loses much of its attraction, and, on the contrary, the charge of the molecule seems a more fundamental characteristic.

In regard to the electrophoresis of proteins the foregoing sections do not lose their interest. In fact, in this case there is an additional problem. If the zeta potential has been evaluated from electrophoretic data, it must be converted into a value for the charge of the particles. And apart from other complications still to be mentioned, evaluating the charge of the particles is essentially more difficult than evaluating the zeta potential. In the case of the zeta potential, the value of the radius of the particles enters into the calculations (see Figs. 1, 4, 5, and 6) as a correction factor, which only changes logarithmically with the dimensions of the particles. For a given zeta potential, however, the particle charge is proportional to the radius (small  $\kappa a$ ) or the surface (large  $\kappa a$ ) of the particle. Consequently the charge is very sensitive to the right choice of the radius and it is by no means easy to determine this radius or an equivalent radius, if the particle is known to be nonspherical.

A second difficulty in interpreting electrophoresis in terms of charge is based upon the fact that in principle an electrokinetic experiment is only informative on the charge of the particles within the surface of shear. This charge, however, is not necessarily identical with the total charge of the particle, just as in general the zeta potential is not always identical with the total potential drop between the particle and the bulk of the liquid. Part of the counterions may be present within the surface of shear, thereby reducing the electrophoretic charge below the charge as determined analytically for example, by titration. This effect may be expected to be especially large in high concentrations of electrolyte, where the double layer is very much compressed. In very dilute solutions, on the

contrary, the double layer is so extended that only a negligible part of its charge is present near the surface of the particles and thus might be included within the surface of shear.

## 2. Spherical Particles

If, for a moment, we leave the above-mentioned difficulties, it is possible to formulate a relation between charge and zeta potential, or between charge and electrophoretic mobility.

For a spherical particle of radius  $a$ , the charge  $Q$  can be simply expressed by noting that it is equal to the opposite of the total charge of the diffuse double layer:

$$Q = - \int_a^\infty \rho \cdot 4\pi r^2 dr = \int_a^\infty \frac{\epsilon}{4\pi} \cdot \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) \cdot 4\pi r^2 dr$$

$$= - \epsilon a^2 \left( \frac{d\psi}{dr} \right)_{r=a} \quad (20)$$

Applying the approximative equation of Debye and Hückel for the potential in the double layer:

$$\psi = \zeta \cdot a \cdot e^{-(a-r)/r} \quad (21)$$

which is allowed when the zeta potential is small,  $d\psi/dr$  in equation (20) may be transformed into:

$$\left( \frac{d\psi}{dr} \right)_{r=a} = - \frac{\zeta}{a} (1 + \kappa a) \quad (22)$$

leading for the charge, to:

$$Q = \epsilon \zeta a (1 + \kappa a) \quad (23)$$

For large particles the charge density,  $\sigma$ , may be important:

$$\sigma = \frac{\epsilon \zeta}{4\pi a} (1 + \kappa a) \quad (24)$$

which for very large values of  $a$  transforms to the equation for the charge density of flat surfaces:

$$\sigma = \frac{\epsilon \zeta \kappa}{4\pi} \quad (25)$$

Two important corrections to equation (23) have to be considered. The first one concerns the case in which  $\zeta$  is not small, so that the approximation of Debye and Hückel:

$$\Delta\psi = \kappa^2\psi$$

must be replaced by the complete equation:

$$\Delta\psi = \kappa^2 \frac{kT}{e(z_+ + z_-)} (e^{z_+ e\psi/kT} - e^{-z_- e\psi/kT}) \quad (26)$$

Unfortunately equation (26) cannot be integrated for a case of spherical symmetry. Müller (49) has given numerical integrations for a number of values of  $\kappa a$  and  $\zeta$  from which the relation between charge and potential can be derived. Gronwall, LaMer, and Sandved (30) and LaMer, Gronwall, and Greiff (42) have solved equation (26) in a series of ascending powers of the charge of the central particle. Numerical values of the coefficients of the first to fifth (symmetric electrolytes) or third (unsymmetric electrolytes) power of the charge are available from their work.

Gorin (24) also applied the work of Gronwall, LaMer, and Sandved to find the correction for larger  $\zeta$  potentials but his equation in the original paper as well as in the book by Abramson, Gorin, and Moyer (4), is inconsistent, as it contains a sum of two quantities of which one has a zero dimension and the other the dimension of velocity.

In Table IV some values of the quantity  $f$  are given, this being the quotient of the charge calculated according to Müller's or LaMer's method (which lead to practically identical results) to the charge calculated in accordance with the approximate equation (23).

In Müller's terminology factor  $f$  is given by:

$$f = \frac{\varphi'(y)}{\varphi(y)} \cdot \frac{y}{1 + \frac{1}{y} \left( \frac{\sum c_i z_i^2}{\sum c_i} \right)^{1/2}}$$

Gronwall, LaMer, and Sandved give the following relation between the  $\zeta$  potential and charge  $Q$ :

$$\zeta = \sum_{m=1}^{\infty} \left( \frac{Q}{\epsilon a} \right)^m \left( - \frac{e}{kT} \right)^{m-1} \cdot \psi_m(\kappa a) \quad (27)$$

in which:

$$\psi_1(x) = \frac{1}{1+x}$$

$$\psi_2(x) = \frac{c_+ z_+^3 - c_- z_-^3}{c_+ z_+^2 - c_- z_-^2} X_2(x)$$

$$\psi_3(x) = \left( \frac{c_+ z_+^3 - c_- z_-^3}{c_+ z_+^2 + c_- z_-^2} \right)^2 X_2^*(x) + \frac{c_+ z_+^4 + c_- z_-^4}{c_+ z_+^2 + c_- z_-^2} X_3(x)$$

$$\psi_6(x) = z^4 X_6(x), \text{ for symmetrical electrolytes only.}$$

The functions  $X(x)$  are available in tabular form (30,42). Correction factor  $f$  now becomes:

$$f = Q(\text{Eq. 27})/Q(\text{Eq. 23})$$

Unfortunately the calculations of Müller and Gronwall *et al.* extend only to relatively small values of  $\kappa a$ . For very large values of  $\kappa a$  the relation between charge and potential can be approximated by the unidimensional case of equation (26), which can be solved exactly, leading to equation (28) for charge density  $\sigma$ , and equation (29) for  $f$ .

$$\sigma = \frac{\epsilon \kappa}{4\pi} \frac{kT}{e} (2)^{1/2} \left( \frac{\exp(z_- e\zeta/kT) - 1}{z_-(z_+ + z_-)} + \frac{\exp(-z_+ e\zeta/kT) - 1}{z_+(z_+ + z_-)} \right)^{1/2} \quad (28)$$

$$f = \frac{kT}{e\zeta} (2)^{1/2} \left( \frac{\exp(z_- e\zeta/kT) - 1}{z_-(z_+ + z_-)} + \frac{\exp(-z_+ e\zeta/kT) - 1}{z_+(z_+ + z_-)} \right)^{1/2} \quad (29)$$

It is seen in Table IV that the corrections increase with increasing  $\kappa a$ , increasing zeta potential, and increasing valency of the counterions. For  $e\zeta/kT < 1$ , that is, for zeta potentials smaller than 25 mv., and for monovalent electrolytes, the corrections remain under 5%.

TABLE IV

$f = Q_{\text{exact}}/Q_{\text{approx}}$  for Different Values of  $\kappa a$  and  $\zeta$   
For a Sphere with Radius  $a$  Å., the Charge  $Q_{\text{exact}}$  is Equal to  
 $0.1395 a(1 + \kappa a)(e\zeta/kT)f$  at 25°C.

$\kappa a$ values	$e\zeta/kT$			
	0	1	2	3
1-1 electrolyte				
$\kappa a = 0$	1	1	1	1
0.3	1	1.004	1.019	1.048
0.6	1	1.010	1.041	1.107
1.0	1	1.015	1.063	1.14
2.0	1	1.023	1.13	"
3.0	1	1.029	1.17 <sup>a</sup>	"
$\infty$	1	1.042	1.17 <sub>5</sub>	1.42
2-1 electrolyte				
$\kappa a = 0$	1	1	1	1
0.2	1	1.022	1.064	1.146
0.4	1	1.05	1.19	1.7
0.7	1	1.09	1.4	"
1.0	1	1.12	"	"
$\infty$	1	1.30 <sub>7</sub>	2.07 <sub>9</sub>	3.88

<sup>a</sup> No data available.

One might doubt whether it is consistent to use these data for the charge at high potentials when the zeta potential is calculated from an

electrophoresis equation like Henry's or Overbeek's, which are only valid for low potentials. The answer is that Henry's equation is not very sensitive to the exact course of the potential curve. Higher potentials act as if the double layer were more compressed, as if  $\kappa a$  were somewhat larger. In the equations of Overbeek, more terms of the development of equation (26) have been included in the correction terms so that Table IV may indeed be directly combined with the zeta potential as calculated from electrophoresis.

Another correction of equation (23) of a somewhat more speculative character has been given by Gorin (25). In all developments given up to this point, the electrolytic ions have been considered to be point charges,

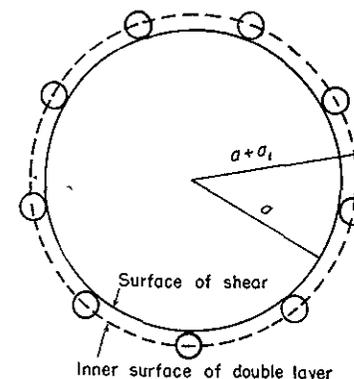


Fig. 7. Spherical particle with counterions showing the difference between surface of shear and limiting surface of the charge of the double layer.

which can approach the surface of the particles to infinitesimally small distances. In 1923 Stern (64), in his theory of the electrocapillary curve, indicated how a correction for the finite dimensions of the ions could be applied. In the same paper he took account of a specific adsorption potential for the ions of the double layer and of the fact that for the ions, which are very near to the surface, the dielectric constant is much lower than that in the bulk of the solution. Gorin applied a similar idea to the interpretation of electrophoresis, using, however, a much simpler theory than that of Stern, in which he took account only of the finite dimensions of the ions, leaving aside the other corrections introduced by Stern.

In Figure 7 a spherical particle has been sketched, surrounded by a number of counterions at the distance of closest approach. The ions of the diffuse part of the double layer have not been indicated in the figure. The surface of shear is formed by a sphere of radius  $a$  (to be determined, for example, from diffusion experiments). The charge of the double layer is

located between the radii  $(a + a_i)$  and  $\infty$ ; the shell between  $a$  and  $(a + a_i)$  is free of charge.

With this picture the relation between charge and potential is easily found and turns out to be:

$$Q = \epsilon \zeta a \left[ \frac{1 + \kappa(a + a_i)}{1 + \kappa a_i} \right] \quad (30)$$

in which  $Q$  is the total charge enclosed within the surface of shear and  $\zeta$  the potential at that surface.

Compared with equation (23), this new equation gives a correction factor in the charge equal to:

$$f = \frac{1 + \kappa(a + a_i)}{(1 + \kappa a)(1 + \kappa a_i)} \quad (31)$$

Assuming for  $a_i$  a value of 2.5 Å. and for  $a$ , alternatively, 25 Å. (for example, a protein molecule with a molecular weight of the order of 40,000) and  $\infty$  (flat surface), the correction factor has been tabulated for different values of the ionic strength in Table V. The influence of the finite dimensions of the ions is seen to result always in a decrease of the charge (the more pronounced, the higher the ionic concentrations). In contrast to the correction mentioned in Table IV the influence of the ionic dimensions is independent of the zeta potential and should be taken into account even for very weakly charged particles.

TABLE V

Correction Factors ( $f = Q_{\text{exact}}/Q_{\text{approx}}$ ) for an Ionic Radius of 2.5 Å.

$\omega = \frac{1}{2} \sum c_i z_i^2$	$\kappa a_i$	$f$ for $a = 25 \text{ \AA.}$	$f$ for $a = \infty$
0.00001	0.00259	0.99994	0.9974
0.0001	0.00819	0.9994	0.992
0.001	0.0259	0.995	0.975
0.005	0.0579	0.980	0.945
0.01	0.0819	0.966	0.924
0.02	0.1159	0.944	0.896
0.05	0.1831	0.899	0.846
0.1	0.2592	0.851	0.794
0.2	0.3662	0.789	0.732

Combination of equation (30) or (31) with an electrophoretic equation like Henry's, which has been derived without taking account of the dimensions of the ions, is nevertheless allowed because closer inspection shows that by Gorin's correction not only has the value of  $\zeta$  for a given

charge been increased by a factor  $1/f$ , but the potential at any point of the double layer has been increased in the same proportion (provided that  $\kappa a_i \ll 1$ ).

A difficulty in the application of equation (30) is the choice of radius  $a_i$ . There is no accord in the literature on the values of radii of hydrated ions (which should be used here), and even if the particle as a whole is spherical its surface will certainly contain local hills and valleys of atomic dimensions, and by going into the valleys the counterions can approach the average surface of shear at a shorter distance than would follow from their radii.

So probably the best thing to do at the moment is to consider the ionic radii  $a_i$  as an additional parameter whose value must be determined by experiments and cannot be predicted without a far greater knowledge than we now have on the constitution and interaction of surfaces of particles in electrophoresis.

### 3. Nonspherical Particles

In practice it will seldom occur, except in the case of emulsions, that the particles are exactly spherical. Unfortunately there are no theoretical investigations on the electrophoresis of ellipsoids of a moderate ratio (say 1:2 or 1:3) of the long and short axis. The only nonspherical forms on which data are available are a flat surface and infinitely long cylinders, as has been mentioned in Section III. The best way of handling nonspherical particles now is to assume that electrophoresis may be represented as that of cylinders of finite length, neglecting the end effects. The degree of validity of this approximation, however, is difficult to estimate.

The additional problem of evaluating the charge of the cylinder when the zeta potential is known has been solved by Gorin (27). Applying the approximation of Debye and Hückel, the charge  $Q$  of a cylinder of length  $l$  and radius  $a$  is given by:

$$Q = \epsilon \zeta \left( \frac{1}{2} l + a \right) \kappa a \frac{K_1(\kappa a)}{K_0(\kappa a)} \quad (32)$$

in which  $K_0$  and  $K_1$  are Bessel functions for which tables are available.

For very large particles, the situation is more favorable. The zeta potential can be found, as treated in Section III from Smoluchowski's equation (6), and the charge density on the surface by application of the equation for flat surfaces (Eqs. 25 and 28). These equations may be useful in the interpretation of the electrophoresis of microscopic particles, which may or may not be covered with a layer of proteins.

For particles that are very small compared to the extension of the double layer again the problem is simpler. Irrespective of the form of the particles, the symmetry of the double layer is practically spherical and all our developments for spherical particles may be applied. The equivalent radius of the particle necessary to estimate the charge according to equation (23) may be taken from diffusion data. Unfortunately, measurements on small particles in dilute solutions where the charge of the particles is known from another, independent, method are very rare. The moving boundary technique of Burton, as modified and ameliorated by Tiselius, and which is especially adapted to small particles like protein molecules, is unsuitable for measurements in systems containing little or no electrolyte. The microscope method, on the other hand, which is easiest to handle in solutions of low conductivity, is restricted by the demand of visibility in the microscope or ultramicroscope to comparatively large particle dimensions. It would certainly be of interest to investigate protein systems, nearly free of electrolyte by the Hittorf method of determining electrophoretic mobility.

#### 4. Applications

The application of the relation between charge and zeta potential to "inert" surfaces by Abramson and Müller (3) is very well known. They find that for these surfaces (oil, graphite,  $\text{SiO}_2$ , etc.) the charge as a function of the electrolyte concentration can be represented by a curve resembling very much an adsorption isotherm. Although the accuracy of the  $\zeta$  values at the lower concentrations may be open to doubt (8,9), the fact that the charge of the surface increases with increasing concentration of electrolyte has been established by independent means. De Bruyn (19) and Kruyt and Klompé (40) found, by analytical determinations, that the addition of any electrolyte produced an increase of the charge of silver iodide. This fact, however, should not be interpreted as a specific adsorption of one of the added ions. As soon as ionic equilibria between the liquid and the material of the suspended particles are possible, the potential difference between surface and liquid is fixed (see Sect. III). The zeta potential will be a more or less accurate image of this potential difference, and the increase of the charge can be explained by the decreased thickness of the double layer, more charge being necessary to produce the same potential drop over a shorter distance.

In a very accurate investigation of the zeta potential of glass, Rutgers (58) too finds that  $\zeta$  can be very well interpreted as the potential of an ex-

change electrode, the charge density being a variable of only secondary importance, which adapts itself to the potential and thickness of the double layer.

In the case of proteins, interpretation of electrophoresis in terms of charge seems more promising because, in this case, the electrophoretic charge can be compared to the analytical charge as determined by titration.

The electrophoretic data on proteins (and other hydrophilic colloids) fall in two categories: the mobility of the free protein molecules can be determined; on the other hand, the mobility of inert particles covered by adsorption with protein can be measured.

*A priori* one would not expect a simple relation to exist between the mobilities of free and adsorbed protein, because the mobility of the adsorbed protein should depend upon the area covered by one molecule and upon the dissociation properties in the adsorbed form, which might be different from that of the free protein. Even if one assumes that the spreading area is such that—at the same pH—the charge densities (or the zeta potentials) of free and of adsorbed protein are identical, the mobility of the free protein should be considerably lower than that of the adsorbed one, because  $\kappa a$  for the free protein is comparatively small and the Henry correction important.

Nevertheless, in many cases, the two mobilities are nearly identical, a fact that has been pointed out by Abramson (1,2,4) on several occasions. Even if by adsorption a shift of the isoelectric point is found, as is the case for egg albumin, the slope of the *u* versus pH curve is the same in both cases. Abramson (2) expressed this curious fact in a very pregnant way by implying that "on adsorption certain proteins take  $\kappa a$  with them."

A satisfactory explanation of this fact has not been given. A supposition compatible with these experiments is that the form of the free protein molecule is not at all spherical, but more like a flat disk in which the polypeptide chains are parallel to the surface of the disk, the hydrophobic side chains being turned to the interior and the hydrophilic ones to the outside. In adsorption the protein should unfold, so that the hydrophobic chains are attached to the adsorbent, the hydrophilic chains being turned to the water. This supposition would imply that the free protein molecule would have a surface of low curvature and behave more or less like a flat surface with  $\kappa a \rightarrow \infty$ . A test of this supposition would be formed by a comparison of the electrophoretic mobility of the adsorbed and the free form at very low ionic strength, where the double layer around the free protein would be

nearly spherical, thereby depressing the mobility as compared to that of the adsorbed form.

### 5. Comparison of Electrophoretic Charge with Charge Determined by Other Means

Apart from the calculation of the charge from electrophoresis, in the case of proteins, at least, two other methods can be used to determine the charge.

The most straightforward method is the determination of the charge from titration data. The titration curve of a protein gives us the number of hydrogen ions taken up or given off by a protein molecule in given circumstances of pH and ionic strength. With each hydrogen ion taken up, the charge increases by  $4.8 \times 10^{-10}$ e.s.u.

Another method has been worked out by Adair and Adair (5). It consists in the calculation of the charge from Donnan equilibria. Although in principle this method looks very attractive because it should include the influence of ions other than  $H^+$  ions, it should not be forgotten that especially in more concentrated solutions the interpretation of Donnan equilibria entails corrections for activity coefficients, which are difficult to estimate exactly.

Tiselius and Svensson (67) determined the electrophoretic velocity of egg albumin at a constant pH of 7.10 but different values of the ionic strength and calculated the charge by application of Henry's equation combined with our equation (23), assuming  $a = 27.5 \text{ \AA}$ . as the radius of the molecule.

Table VI shows a comparison of the charge thus calculated from electrophoresis and as determined by Adair and Adair from membrane potentials. The agreement is very satisfactory.

A direct comparison of these data with other titration data cannot be given because the titrations, e.g., those of Cannan, Kibrick, and Palmer (16), were made in sodium chloride solutions, whereas the data of Tiselius and Adair are for phosphate buffers. The last column of Table VI gives the charge as determined by titration data. The titration curves have been shifted, so that they pass through the electrophoretic isoelectric point. At low values of the ionic strength, the agreement among the three methods is good, but, at higher values of the ionic strength, the charge as determined by titration is markedly higher than that by the other two methods.

This difference between electrophoresis charge and charge by titration is still more pronounced in an investigation by Longworth (44). He compared titration data and electrophoresis of egg albumin over a wide range

TABLE VI

Comparison of the Charge of a Molecule of Egg Albumin at pH 7.10 Expressed in the Number of Elementary Charges by Three Different Methods

Ionic strength	$u \times 10^4$	$sa$	$Q$ from electrophoresis	$Q$ from membrane potentials	$Q$ from titration curves
0.01	1.16	0.88	12	12	13.8
0.02	(1.00)	1.24	12.4	12.6	14.7
0.05	0.760	1.95	12	13.1	16.0
0.10	0.670	2.75	13.2	13.8	17.0
0.20	0.570	3.9	14.1	15.1	19.1

of pH using only buffers with monovalent ions and, although a beautiful parallelism exists between the two sets of data, the electrophoresis charge is only 60% of the charge by titration (see Fig. 8).

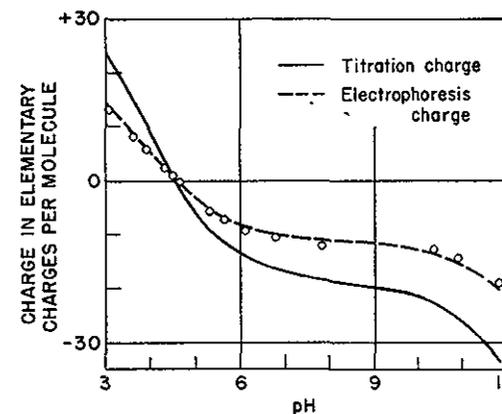


Fig. 8. Charge by titration and electrophoresis charge of egg albumin (44). The broken curve is found from the continuous curve by multiplying the ordinates by 0.60. Ionic strength = 0.1.

In Figure 8 the electrophoresis charge has been calculated using Henry's equation and our equation (23). If the relaxation effect and the correction for large potentials (see Table IV) are taken into account, the electrophoresis charge is increased by less than 5%. Introduction of the Gorin correction for the finite dimension of the ions (Table V) gives a decrease of the charge by some 15%, whereas if the particles are considered to be cylindrical rods instead of spheres the charge is increased by about 20% (4, p. 154). Neither correction is sufficiently large to reconcile the difference between the two sets of data.

The larger difference as compared to the data of Tiselius and Svensson must be ascribed to their use of phosphate buffers, which apparently increase the electrophoretic mobility substantially. This difference cannot be ascribed to the influence of the relaxation effect, which in the circumstances used here is never larger than 1 or 2%. A specific adsorption of phosphate ions seems the more plausible explanation (63).

A similar comparison between the titration curves and the electrophoretic mobility at an ionic strength of 0.02 has been made by Cannan, Palmer, and Kibrick (17). Here again the charge by titration is about 20% higher than the electrophoresis charge and the difference cannot be accounted for by the correction factors of Tables IV and V, nor by the relaxation effect. Gorin and Moyer (28) mention that by their theory they find a quantitative accord between the two sets of data. It is not clear, however, whether they mean the introduction of the assumption that the particle is not spherical but more nearly cylindrical, or their theory that the binding of hydrogen ion is independent of the ionic strength (see below). Both assumptions would be expected to bring the two data nearer to each other.

For serum albumin B the situation is similar to that of egg albumin. Mobility data of Keckwick (37) and Gorin and Moyer (28) can be compared to titration data of Gorin and Moyer (28). For small values of the ionic strength, the agreement between charge by titration and electrophoresis charge is satisfactory. At higher concentrations of electrolyte (ionic strength 0.02 and 0.1), the charge by titration is markedly higher than the electrophoresis charge.

The difference between charge by titration and electrophoresis charge has been interpreted in two different ways. Cannan, Kibrick, and Palmer (16), and Longworth (44) assume that the titration curves give essential information on the hydrogen ion bound to or released by the protein. At higher ionic concentration, however, an important absorption of counterions exists which diminishes the electrophoresis charge. Gorin and Moyer (28), on the contrary, assume that the binding of hydrogen ion is essentially independent of ionic strength, so that at any ionic strength mobility data form a direct measure of hydrogen binding. But the charge by titration is apparently too large, because not only  $H^+$  ions but also undissociated molecules of acid or base are bound to the protein. This assumption seems a bit artificial, especially since the difference in titration curves at different values of the ionic strength can be explained by the electrostatic interaction of the charges on the protein. This interaction is diminished at high ionic strength due to the screening effect of the double layer.

The binding of counterions assumed by Longworth and Cannan need not necessarily be ascribed to specific interaction. It seems possible that

at high ionic strength a part of the counterions is present within the surface of shear (which also contains a certain amount of water of hydration), and by a simple steric effect diminishes the electrophoresis charge

It cannot, however, be denied that, in the cases mentioned above, which are the only ones forming a real quantitative test of the theory of electrophoresis, the situation is still far from satisfactory. It may be hoped that a better insight in the adsorption of ions other than  $H^+$  and a more accurate knowledge of the form of the proteins will bring about a more complete accord between theory and experiments.

## 6. General Conclusions

Since the influence of the relaxation effect has been included in the theory of electrophoresis, the basis for estimating the zeta potential from electrophoretic mobility seems rather sound.

There are, of course, still additional developments to be desired, essentially:

- (1) An extension of the calculation of the relaxation effect to higher values of  $\zeta$ .
- (2) A theory of electrophoresis for particles of other forms especially for ellipsoidal particles and for randomly kinked long chains.
- (3) A well-founded explanation of the equality of electrophoretic mobility of free and adsorbed proteins.

The relation between the charge and the zeta potential, although in principle much easier to formulate than the relation between  $u$  and  $\zeta$ , gives rise to serious difficulties in application, because either the form and dimensions of the particles are not known with sufficient accuracy, or because there really is an essential difference between the electrophoretic and the analytical charge as a consequence of the adsorption of other than hydrogen ions.

The author wants to emphasize a remark made by Booth (11)—that what is most needed in the present state of the theory are better experimental data to compare with the theory. Especially useful information could be derived from:

- (1) Comparisons between electrophoretic and electro-osmotic mobilities of identical surfaces especially at high  $\zeta$  potentials and low values of the ionic strength.
- (2) Comparisons between the electrophoresis of free and adsorbed proteins at low values of ionic strength.
- (3) More data on titration and electrophoresis of the same object, again at low ionic strength.

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