The Interpretation of Electrophoretic Mobilities

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I. Introduction

Electrophoresis experiments are frequently carried out with the purpose of measuring the electrophoretic velocity. The velocity per unit

strength of the applied electrical dc field is called the "electrophoretic mobility" and is a characteristic property of the colloidal system that is being studied.

In this chapter, the electrophoretic mobility (E.M.) will be considered as a given quantity, and the discussion will be limited to the theoretical interpretation of experimental mobilities. In this interpretation, the concept of the electrical double layer plays a central part. This concept is discussed extensively by Overbeek and Lijklema (1) in Vol. I of this book; we shall frequently refer to that discussion.

As an example of a theoretical relation between the E.M. and properties of the double layer, we mention the well-known equation derived by von Helmholtz (2) and improved by von Smoluchowski (3):

$$\frac{U}{X} = \frac{\epsilon \zeta}{4\pi\eta} \tag{1}$$

In Eq. (1), U is the electrophoretic velocity and **X** is the strength of the applied dc field; hence, **U/X** is the electrophoretic mobility, ζ is the electrokinetic potential; ϵ and η represent the dielectric constant and the viscosity coefficient, respectively, of the liquid surrounding the colloid particles.

It has been known a long time that the validity of Eq. (1) is rather restricted, and a considerable amount of theoretical work has been carried out in order to arrive at more general relations between the E.M. and the properties of the double layer.

The older part of this theoretical work was reviewed in 1950 by Overbeek (4). Since then, this subject has been treated in a number of review articles and textbooks. Of these publications, we mention here the reviews written by Booth (5) and by Haydon (6), and the textbooks of Kruyt (7) and of Rice and Nagasawa (8). A number of details occurring in other review articles will not be reported here.

In Section II of this chapter, we shall give a brief description of the various effects that play a part in electrophoresis. Up to the present, a rigorous theory, accounting for all these effects, has been worked out only for a relatively simple model. In this model, the colloidal particle is considered as a rigid sphere surrounded by a Gouy-Chapman double layer. The theory based upon this assumption will be treated in Section III. In Section IV we shall discuss the theoretical work carried out on the basis of less restrictive models, such as nonspherical particles. Finally, Section V will be devoted to the electrophoresis of polyelectrolytes.

II. General Considerations

Shortly after the dc field is applied to the colloidal solution, the system reaches a stationary state in which the velocity of the particles in the direction of the field is constant in time. There are four different forces acting on a particle that is in electrophoretic motion (Fig. 1). The first one
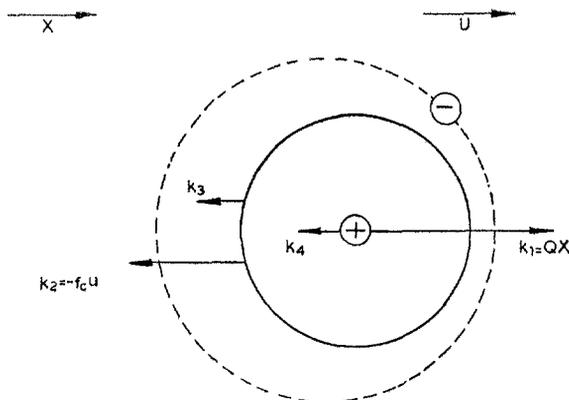
FIG. 1. Forces in electrophoresis.

is the force exerted by the dc field on the charge of the particle. This force, which we shall denote by the vector k_1, can be written

$$k_1 = Q X \qquad (2)$$

where X is the dc field and Q is the charge of the particle. The second force, k_2, is the Stokes friction. It can be expressed as

$$k_2 = -f_c U \qquad (3)$$

where U is the electrophoretic velocity and f_c is the friction coefficient of the colloid particle. For a rigid spherical particle that is large compared to the molecules of the liquid surrounding it,

$$f_c = 6\pi\eta a \qquad (4)$$

where a is the radius of the sphere. For a nonspherical particle, f_c is still proportional to η; the proportionality factor depends on size, shape, and orientation of the particle.

The two remaining forces, k_3 and k_4, are caused by the presence of the small electrolyte ions in the colloidal solution. In the vicinity of a colloid particle, these ions are distributed unequally, with the result that the

liquid has a net charge which is opposite in sign to that on the particle. This is the so-called ionic atmosphere. When the particle is a polyelectrolyte coil there exists, in addition, a similar unequal distribution of ions in the region occupied by the coil.

The electric dc field exerts a force on the ions in the ionic atmosphere. This force is transferred to the molecules of the solvent. The resulting flow of the liquid causes a retarding force, k_3, on the colloid particle. This effect is called "electrophoretic retardation."

Furthermore, the distribution of ions in the vicinity of the particle is deformed when the dc field is applied. This is caused by the fact that the particle moves away from the center of its ionic atmosphere. The Coulomb forces between the charge Q and the ions tend to rebuild the atmosphere in its "proper" place. However, this takes a finite time called the relaxation time. Hence, in the stationary state the center of the ionic atmosphere constantly lags behind the center of the particle. The result is an electrical force, k_4, on the charge of the particle. This force, which is, in most cases, a retarding one, is called "the relaxation effect." In a drained polyelectrolyte coil, the ionic distribution inside the coil is also deformed, which makes the relaxation effect more complicated.

The two effects symbolized by k_3 and k_4 are the same as those defined in the Debye-Hückel theory of the conductivity of strong electrolytes (9). In this theory, the two forces are calculated separately and then linearly superimposed. For colloid particles, such a linear superposition would lead to a serious error, because in this case the mutual interactions between the two effects are considerable. Hence, for colloid solutions, k_3 must be calculated for a deformed ionic distribution, and in the calculation of k_4, the velocity pattern in the liquid must be taken into account explicitly.

In the stationary state, the sum of all forces acting on the particle is zero:

$$k_1 + k_2 + k_3 + k_4 = 0 \qquad (5)$$

Equations (2), (3), and (5) can be combined to give

$$U = \frac{1}{f_c}(QX + k_3 + k_4) \qquad (6)$$

Generally, the forces k_3 and k_4 are complicated functions of several parameters of the colloidal solution, such as the ζ-potential, the dimensions of the colloid particle, and the charges, concentrations and mobilities of the small ions in the solution. In a number of limiting cases, most of which will be discussed in Section III, rather simple expressions for the electrophoretic mobility are applicable.

In order to calculate the forces k_3 and k_4, one needs a quantitative description of the electrical double layer. In most calculations, the theory of Gouy (10, 11) and Chapman (12) has been used. This theory leads to the so-called Poisson-Boltzmann equation:

$$\text{div grad } \psi = -\frac{4\pi e}{\epsilon} \sum_i n_i z_i \exp\left(-\frac{z_i e\psi}{kT}\right) \qquad (7)$$

where ψ is the electric potential in the double layer, e is the elementary charge, k is Boltzmann's constant, and T is the absolute temperature; n_i and z_i are the average concentrations and the valences, respectively, of the small ions in the double layer. A more detailed discussion of the Gouy-Chapman theory, including a derivation of Eq. (7), can be found in Vol. I (1). In an external dc field, the potential distribution is disturbed (relaxation effect) and cannot be described by Eq. (7). But even in calculations where the relaxation effect is accounted for, Eq. (7) serves as a useful first approximation. For the limiting case $z_i e\psi/kT \ll 1$, the Poisson-Boltzmann equation can be reduced to its linear form

$$\text{div grad } \psi = \kappa^2 \psi \qquad (8)$$

where

$$\kappa^2 \equiv 4\pi e^2 \sum_i n_i z_i^2 / \epsilon kT \qquad (9)$$

Equation (8) was first introduced by Debye and Hückel (13) and has also been used in some electrophoresis theories (cf. Section III). The quantity $1/\kappa$ has the dimension of length and is a measure of the thickness of the double layer.

At the end of this section we wish to emphasize a few important features of the model that is used in all electrophoretic theories, at least for rigid particles. It is generally assumed that, when a rigid particle moves through a liquid, a thin layer of liquid adjacent to the wall of the particle remains completely fixed to it. The boundary enveloping the fixed layer of liquid is called "the surface of shear." Whereas ψ_0 is defined as the potential difference across the entire double layer, ζ is the potential difference across its mobile part; in other words, ζ is the value of ψ at the surface of shear. Usually, ζ has the sign of ψ_0 but a smaller absolute value. Furthermore, the symbol Q [cf. Eq. (2)] denotes all the charge that is present within the surface of shear. As this may (and usually does) include some of the bound counterions, Q may be smaller than the particle charge found, for instance, by titration. In this chapter, we shall use the term "electrokinetic charge" for Q. Finally, we observe that the symbol

a in Eq. (4) can be more precisely defined as the distance from the particle to the surface of shear.

III. Theory for a Rigid Spherical Particle

A. HISTORICAL INTRODUCTION

The finding of a relation between the electrophoretic mobility and the properties of the double layer is a classical problem in colloid science. The Helmholtz-Smoluchowski Eq. (1) can be considered as the oldest solution of this problem. It is not limited to any special particle shape (cf. Section IV,G). The derivation of Eq. (1) has been discussed in several other publications (see e.g., References 4, 7, 8, 14) but we shall review it here because it illustrates so many of the ideas discussed in this chapter.

If the particle is a nonconductor of electricity and the electric double layer is thin compared to the radius of curvature of any part of the particle surface, the directions of the external field and of the flow of the liquid are parallel to each other and to the wall of the particle in the entire double layer. Consider a portion, *S,* of the surface of shear which is so small that its curvature may be neglected and let *x* be the distance from this surface (Fig. 2). Suppose the particle is positively charged and moves to the right with a velocity **U**, parallel to the direction of the external field, **X.** In the vicinity of the particle, the lines of force of the external field are distorted and are symbolized by the vector **E**; the
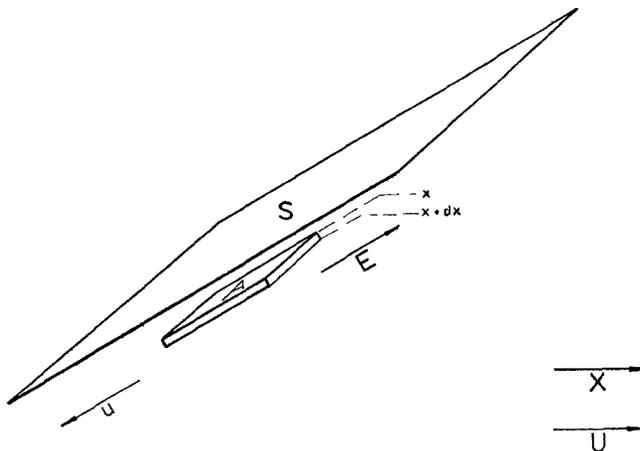
FIG. 2. Diagram for calculation of von Smoluchowski.

velocity of the liquid *with respect to the particle* is denoted by **u.** In the double layer around a positive particle, **E** and **u** are parallel but have opposite directions.

Let us now consider the forces acting on a volume element of liquid having an area A (parallel to the wall) and an infinitesimal thickness dx (perpendicular to the wall). First, as adjacent portions of the liquid move with different velocities, the volume element is subject to viscous forces. Its upper surface is acted upon by a force

$$-A \left(\eta \frac{d\mathbf{u}}{dx} \right)_x \tag{10}$$

and its base by a force

$$A \left(\eta \frac{d\mathbf{u}}{dx} \right)_{x+dx} = A \left(\eta \frac{d\mathbf{u}}{dx} \right)_x + A \left[\frac{d}{dx} \left(\eta \frac{d\mathbf{u}}{dx} \right) \right]_x dx \tag{11}$$

A force having the same direction as that of **E** is considered to be positive ($d\mathbf{u}/dx < 0$); the right-hand side of Eq. (11) is obtained from the left-hand side by means of a Taylor expansion. The electrical force acting on the ions (and, hence, on the liquid) in the volume element is

$$\rho \mathbf{E} A \, dx \tag{12}$$

where ρ is the charge density in the liquid. This "volume force," which causes the electrophoretic retardation, was already discussed in Section II; in our case it is negative because ρ is negative. By means of Poisson's equation,

$$\frac{d}{dx} \left(\epsilon \frac{d\psi}{dx} \right) = -4\pi\rho \tag{13}$$

the charge density can be expressed in terms of ψ, the electric potential of the double layer.

In the stationary state, the sum of all forces is zero; hence, by combination of Eqs. (10) to (13),

$$\frac{d}{dx} \left(\eta \frac{d\mathbf{u}}{dx} \right) - \frac{\mathbf{E}}{4\pi} \frac{d}{dx} \left(\epsilon \frac{d\psi}{dx} \right) = 0 \tag{14}$$

for any value of x. Strictly speaking, Eq. (14) should contain a third term accounting for differences in hydrostatic pressure in the liquid [cf. Eq. (25)] but von Smoluchowski (3) has shown that in this special case the pressure term has no effect on the result of the derivation.

We now multiply all terms of Eq. (14) with the variable distance x and integrate the result over the region $0 < x < \delta$, where δ is a value of

x just outside the range of the double layer. Since $\mathbf{E}$ does not depend on x in this region, we obtain

$$\int_0^\delta x \frac{d}{dx} \left(\eta \frac{d\mathbf{u}}{dx} \right) dx = \frac{\mathbf{E}}{4\pi} \int_0^\delta x \frac{d}{dx} \left(\epsilon \frac{d\psi}{dx} \right) dx$$

Integration by parts leads to

$$x \left(\eta \frac{d\mathbf{u}}{dx} \right) \Big|_0^\delta - \int_0^\delta \eta \frac{d\mathbf{u}}{dx} \, dx = \frac{\mathbf{E}}{4\pi} \left[x \left(\epsilon \frac{d\psi}{dx} \right) \Big|_0^\delta - \int_0^\delta \epsilon \frac{d\psi}{dx} \, dx \right] \qquad (15)$$

Since, at $x = \delta$, both $d\mathbf{u}/dx$ and $d\psi/dx$ are zero, the first terms on either side of Eq. (15) vanish. Solving the remaining integrals (assuming that ϵ and η are independent of x), we obtain

$$\eta \, \mathbf{u} \, \Big|_0^\delta = \frac{\mathbf{E}\epsilon}{4\pi} \, \psi \, \Big|_0^\delta$$

At the surface of shear ($x = 0$), $\mathbf{u} = 0$ and $\psi = \zeta$ (both by definition); at $x = \delta$, $\psi = 0$. Hence, just outside the double layer,

$$\mathbf{u} = -\frac{\epsilon\zeta}{4\pi\eta} \, \mathbf{E} \qquad (16)$$

By considering the properties of $\mathbf{u}$ and $\mathbf{E}$ in the region outside the double layer (the liquid is incompressible and the charge density is zero) it can be shown (3) that in this region $\mathbf{u}$ and $\mathbf{E}$ are everywhere parallel and proportional to each other and that the proportionality factor is the same everywhere. In other words, Eq. (16) is also valid at a large distance from the particle, where $\mathbf{u} = -\mathbf{U}$ and $\mathbf{E} = \mathbf{X}$ (both by definition). It follows that

$$\frac{\mathbf{U}}{\mathbf{X}} = \frac{\epsilon\zeta}{4\pi\eta} \qquad (17)$$

which is identical with Eq. (1). It is of interest to note that Eq. (17) is derived without any specific assumption concerning the distribution of ions in the double layer; only Poisson's equation is required. We further observe that the relaxation effect was not considered in the derivation (see, however, Section III,G).

The Debye-Hückel theory of strong electrolytes led to a further development of the theory of electrophoresis. In 1924, Hückel (15) published a detailed calculation of the electrophoretic retardation force ($\mathbf{k}_3$) acting on a spherical particle. His result was

$$\mathbf{k}_3 = (\epsilon\zeta a - Q)\mathbf{X} \qquad (18)$$

When we combine this result with Eq. (6), substituting Eq. (4) and neglecting k_4, we obtain

$$\frac{U}{X} = \frac{\epsilon \zeta}{6\pi\eta} \tag{19}$$

An elementary derivation of Eq. (19) was given by Rutgers and Overbeek (16), on the basis of a simple treatment of electrophoretic retardation introduced by Onsager (17). From the paper of Rutgers and Overbeek it follows that Eq. (19) can be derived without considering the detailed structure of the double layer; only Poisson's equation is required.

The apparent contradiction between Eqs. (17) and (19) was resolved by Henry (18), who gave a critical analysis of the assumptions underlying these equations. As we have mentioned, von Smoluchowski had assumed that, in the entire double layer, the direction of the dc field is parallel to the particle surface. Hückel's treatment contains the assumption that, everywhere in the double layer, the lines of force run straight from anode to cathode. Therefore, Hückel arrived at a higher value of the electrophoretic retardation force than did von Smoluchowski.

The deformation of the applied field by the presence of the particle was accurately taken into account in Henry's calculation of k_3. The shape of the field depends on the electrical conductivities of the particle and of the liquid surrounding it. In this section, we consider only an insulating spherical particle. For this case, Henry's result can be written

$$\frac{U}{X} = \frac{\epsilon \zeta}{6\pi\eta} f_1(\kappa a) \tag{20}$$

where κ is given by Eq. (9) and a is defined at the end of Section II. The dimensionless product κa is a measure of the ratio between the particle radius and the thickness of the double layer. In the limiting case $\kappa a \rightarrow \infty$ (i.e., when the double layer is very thin compared with the radius), $f_1(\kappa a) = \frac{3}{2}$ and Henry's result is reduced to the Helmholtz-Smoluchowski Eq. (17). When $\kappa a \rightarrow 0$, $f_1(\kappa a) = 1$ and the result of Hückel, Eq. (19), is obtained. A graph of the function $f(\kappa a) = \frac{2}{3} f_1(\kappa a)$, as well as analytical expressions for this function, can be found in Henry's paper (18). For future reference, we mention that Henry's calculation was based upon the linear equation (8).

In all calculations mentioned so far, the relaxation effect (k_4) was neglected. In the decade between 1928 and 1938 several authors (19–23) have treated the relaxation effect for colloidal solutions. A critical review of these calculations was given by Overbeek (24, 25). Because of the mathematical difficulties, the validity of the results is rather restricted.

More recently, Overbeek (24, 25) and Booth (26, 27) independently

have given detailed treatments of the relaxation effect for a spherical insulating particle. Both authors have used the Gouy-Chapman theory as a first approximation for the description of the ionic atmosphere; the deformation of the atmosphere by the external field (the relaxation effect) was introduced in the higher approximations. A major mathematical problem was caused by the fact that, for a spherical colloid particle, Eq. (7) has no tractable analytical solution, whereas the linear equation (8) is, even as a first approximation, definitely insufficient for obtaining the relaxation effect. As a compromise, both Overbeek and Booth have used series solutions of Eq. (7), of the type given by Gronwall *et al.* (28, 29).

The results of Overbeek and of Booth can be expressed in the form of a power series in the ζ-potential:

$$\frac{U}{X} = \frac{\epsilon\zeta}{6\pi\eta} [f_1(\kappa a) + C_2\zeta + C_3\zeta^2 + C_4\zeta^3 + \cdots] \qquad (21)$$

In Eq. (21), $f_1(\kappa a)$ is the function occurring in Henry's result, Eq. (20); the coefficients C_n are complicated functions of κa and of the valences and the mobilities of the small electrolyte ions. Because of the mathematical complications, only a few terms of the power series could be calculated. Overbeek obtained the coefficients C_2 and C_3, whereas Booth calculated, in addition, C_4; the term $C_4\zeta^3$ is relatively small. The results of the two authors are in good agreement. Additional details can be found in the original publications (24–27), in review articles by Overbeek (4), by Booth (5), and by Haydon (6), and in Section III,D,2 of this chapter. A few important conclusions will be mentioned here. The function between brackets in Eq. (21) is reduced to Henry's function $f_1(\kappa a)$ in the following circumstances: (a) $\zeta \ll 25$ mV (arbitrary values of κa), (b) $\kappa a \ll 1$ (arbitrary values of ζ), and (c) $\kappa a \gg 1$ (arbitrary values of ζ). This implies that the relaxation effect is negligible when one of these conditions is met. For $\kappa a \gg 1$ or $\kappa a \ll 1$, Eq. (21) approaches the same limiting expressions [Eqs. (17) and (19), respectively] as does Henry's equation (20). For the case $\kappa a \gg 1$, this was proven in an elementary manner by Overbeek (4, 30). From Eq. (21) it could be concluded that, for intermediate values of κa (say, $\kappa a = 5$), the relaxation effect gives an important contribution, increasing with increasing ζ-potential. However, because the power series in Eq. (21) is incomplete, the exact magnitude of the relaxation effect remained uncertain.

A recent treatment of the electrophoresis of a spherical particle was published by Pickard (31). His model and basic equations are similar to those of Overbeek (24, 25) and of Booth (26, 27), although they

contain a few additional features. However, because of approximations introduced in certain steps of his calculation, Pickard arrives at a result predicting that U/X is proportional to ζ; this implies that the result does not account for the relaxation effect. More detailed comments on Pickard's paper can be found in a publication by Wiersema et al. (32).

The appearance of electronic computers made it possible to deal more efficiently with the mathematics involved in the theory of electrophoresis. In 1953, Hoskin (33) computed exact solutions of the Poisson-Boltzmann equation (7) for a spherical double layer. Loeb et al. (34) improved and extended the work of Hoskin in such a way that a suitable basis for the numerical computation of the E.M. was obtained. This computation was carried out by Wiersema et al. (32, 35, 36). The fundamental assumptions and the results will be reviewed in Sections III, B through III, E. For more details the reader is referred to the original publications. Reference 36 contains the complete results and a discussion of practical applications; in Reference 32, the emphasis is on mathematical methods.

B. PHYSICAL ASSUMPTIONS

In their computation, Wiersema et al. (36) used the same assumptions as did Overbeek (24, 25). They are as follows: (1) Only a single particle is considered, which implies that the interaction between colloid particles is neglected. (2) It is assumed that the colloidal solution follows Ohm's law; in other words, all terms nonlinear in the dc field are neglected. (3) In the computation of the relaxation effect, the Brownian motion of the colloid particle is neglected. (4) The colloid particle (plus the adjacent layer of liquid that moves with it) is treated as a rigid sphere. (5) The dielectric constant is supposed to be the same everywhere in the sphere. (6) The electric conductivity of the sphere is assumed to be zero. (7) The viscosity coefficient of the liquid surrounding the sphere is assumed to be independent of position. (8) The electrical double layer is described by the Gouy-Chapman theory. This implies, among other things, the following assumptions: (a) the dielectric constant is independent of position; (b) the small electrolyte ions are point charges that interact with the particle through Coulomb forces only; (c) the charge of the sphere is distributed uniformly on its surface. (9) Only one type of positive and one type of negative ions are considered to be present in the solution.

The discussion of these assumptions is postponed to Sections IV and V.

C. MATHEMATICAL EQUATIONS

We shall now give a very brief discussion of the differential equations that were solved in order to obtain the E.M. More details can be found

in the publications of Henry (18), Overbeek (24, 25), Booth (27), and Wiersema *et al.* (32, 35, 36).

First, we have Poisson's equation

$$\text{div grad } \Lambda = \frac{-4\pi\rho}{\epsilon} = \frac{-4\pi e}{\epsilon} (z_+\nu_+ - z_-\nu_-) \qquad (22)$$

In Eq. (22), Λ is the total electric potential, which includes the contributions of the charges on the sphere and in the liquid and of the external field; ν_+ and ν_- are the local ion concentrations in the distorted atmosphere. By writing Poisson's equation in this general form, the relaxation effect is accounted for.

Because there is no space charge within the sphere,

$$\text{div grad } \Lambda_i = 0 \qquad (23)$$

where Λ_i is the electric potential inside the sphere.

The concentrations ν_- and ν_- are governed by two transport equations that can be written in a combined form as follows:

$$\text{div} \left[\mp \frac{\nu_\pm z_\pm e}{f_\pm} \text{grad } \Lambda - \frac{kT}{f_\pm} \text{grad } \nu_\pm + \nu_\pm \mathbf{u} \right] = 0 \qquad (24)$$

where f_+ and f_- are the friction coefficients of the ions, and $\mathbf{u}$ is the velocity of the liquid with respect to the particle. The three terms within the brackets indicate that the ions are transported by migration in the electric field, by diffusion, and by convection, respectively. In a coordinate system fixed to the particle, the divergence of the total flow is zero because, in the stationary state, the ionic distribution around the sphere remains constant in time.

The flow of the liquid is described by the Navier-Stokes equation

$$\eta \text{ rot rot } \mathbf{u} + \text{grad } p + \rho \text{ grad } \Lambda = 0 \qquad (25)$$

where p is the hydrostatic pressure in the liquid and ρ is given by Eq. (22). Equation (25) expresses, in a more general way than does Eq. (14) that, in the stationary state, the forces on a volume element of liquid balance each other.

Finally, because the liquid is incompressible,

$$\text{div } \mathbf{u} = 0 \qquad (26)$$

With the aid of suitable boundary conditions, Eqs. (22) to (26) were solved simultaneously by means of successive approximations, using an IBM 704 electronic computer. As a result, Λ, ν_+, ν_-, $\mathbf{u}$, and p were obtained as functions of position. This leads to detailed expressions for the forces $\mathbf{k}_3$ and $\mathbf{k}_4$ (cf. Fig. 1), which can be substituted into Eq. (6)

n order to find the electrophoretic velocity. The results can be con-
sidered as a completion of the power series given in Eq. (21).

D. RESULTS AND DISCUSSION

1. *Dimensionless Variables*

The results of Wiersema *et al.* (32, 35, 36) were obtained in the form
of tables of the dimensionless quantity E, defined by Eq. (27)

$$E \equiv \frac{6\pi\eta e}{\epsilon kT} \frac{U}{X} \tag{27}$$

where U/X is the E.M. For dilute aqueous solutions at 25°C, $E = 0.7503$
$\times 10^4$ (U/X), when U/X is expressed in square centimeters per volt
per second. The function E was computed for several combinations of
the parameters z_+, z_-, κa, y_0, m_+, and m_-. The quantity y_0 is defined
by Eq. (28):

$$y_0 \equiv \frac{\epsilon \zeta}{kT} \tag{28}$$

For aqueous solutions at 25°C, $y_0 = 0.0389\zeta$, when ζ is expressed in
millivolts. The parameters m_+ and m_- are given by

$$m_\pm \equiv \frac{N_a \epsilon kT}{16\pi\eta} \frac{z_\pm}{\lambda_\pm^0} \tag{29}$$

where N_a is Avogadro's number and λ_+^0 and λ_-^0 are the limiting equiva-
lent conductances of the small ions. These conductances appear as a
consequence of the introduction of the friction coefficients, f_+ and f_-,
in Eq. (24). For aqueous solutions at 25°C, $m_\pm = 12.86$ $(z_\pm/\lambda_\pm^0)$,
when $\lambda_\pm^0$ are given in ohm^{-1} cm^2 equivalent^{-1}.

In the calculations, the colloid particle was assumed to be positively
charged. Consistent sign reversal makes the results applicable to negative
colloids; it will be helpful to remember that the subscript $+$ always re-
fers to co-ions, and the subscript $-$ to counterions.

2. *Analytical Approximations*

In order to facilitate the comparison between the approximate equa-
tions of Section III,A and the computer results of Wiersema *et al.*, we
shall write the approximations in terms of dimensionless variables. By
combination of the Helmholtz-Smoluchowski equation (17) with Eq. (27)
we obtain

$$E = \tfrac{3}{2} y_0 \tag{30}$$

In the same notation, the result of Hückel, Eq. (19), reads

$$E = y_0 \tag{31}$$

Henry's equation (20) can be expressed

$$E = y_0 f_1(\kappa a) \tag{32}$$

The calculation of Overbeek (24, 25) leads to

$$E = y_0 f_1(\kappa a) - y_0^3 [z^2 f_3(\kappa a) + \tfrac{1}{2}(m_+ + m_-) f_1(\kappa a)] \tag{33}$$

for symmetrical electrolytes and to

$$\boldsymbol{E} = y_0 f_1(\kappa a) - y_0^2 (z_- - z_+) f_2(\kappa a) - y_0^3 \frac{z_+ m_+ + z_- m_-}{z_+ + z_-} f_1(\kappa a) \tag{34}$$

for unsymmetrical electrolytes. In Eq. (33), z is the valence of both small ions; Eq. (34) applies to a positively charged colloid particle. Tables and graphs of the functions $f_n(\kappa a)$ can be found in References 4, 24, and 25.

The result of Booth (27) is limited to symmetrical electrolytes and can be written

$$E = y_0 X_1^*(\kappa a) + y_0^3 [z^2 \{X_3^*(\kappa a) + Y_3^*(\kappa a)\} + 3(m_+ + m_-) Z_3^*(\kappa a)]$$

$$+ y_0^4 \{3z(m_+ - m_-) Z_4^*(\kappa a)\} \tag{35}$$

The function $X_1^*(\kappa a)$ is identical with $f_1(\kappa a)$ in Eqs. (32) to (34). Graphs of the functions $X_3^*(\kappa a)$, $Y_3^*(\kappa a)$, $Z_3^*(\kappa a)$, and $Z_4^*(\kappa a)$ are given in Fig. 2 of Booth's paper (27).

3. *Results for 1–1 Electrolytes*

Figure 3 shows the computer results for univalent electrolytes and for $m_+ = m_- = 0.184$ ($\lambda_i^0 = 70$ ohm^{-1} cm^2 equivalent^{-1} in aqueous solutions at 25°C). No data were obtained for $y_0 > 6$ ($\zeta > 150$ mV), because in this region the computer program failed to give convergent results.

In Figs. 4 and 5, some of these computer results are compared with the analytical approximations of Henry (18), of Overbeek (24, 25), and of Booth (27).

From Figs. 3 to 5, the following conclusions can be drawn: (1) The relaxation correction is appreciable and increases sharply with increasing ζ-potential; (2) the relaxation effect is largest for moderate values of κa and is negligible when κa is very small or very large; (3) for intermediate values of κa (say, $5 < \kappa a < 50$), the computer results predict a maximum in the curve of the E.M. vs ζ (this cannot be concluded from Fig. 4, but it does follow from Fig. 3); and (4) for low values of ζ, the approximations of Overbeek (24, 25) and of Booth (27) are quantita-
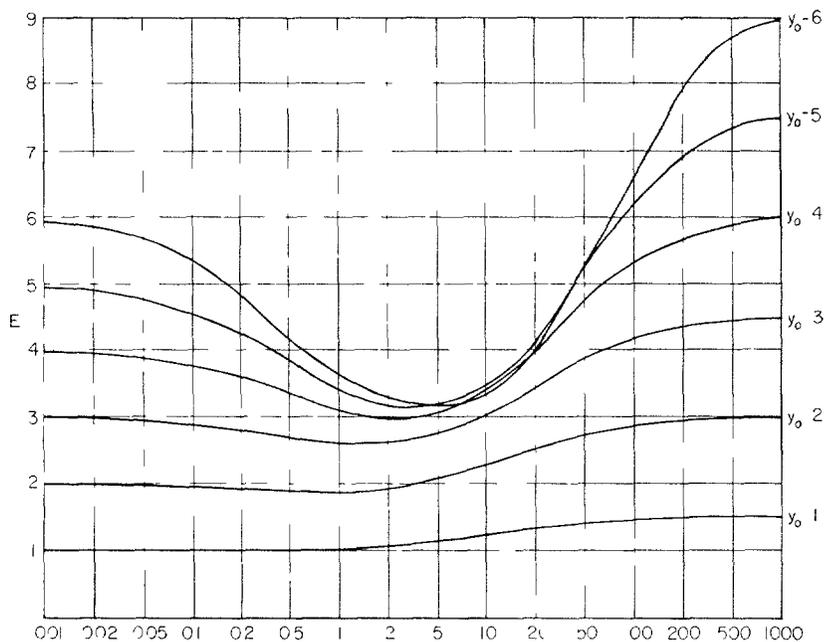
FIG. 3 Plot of E as a function of κa for different values of y_0 ($z_+ = z_- = 1$, $m_+ = m_- = 0\,184$).
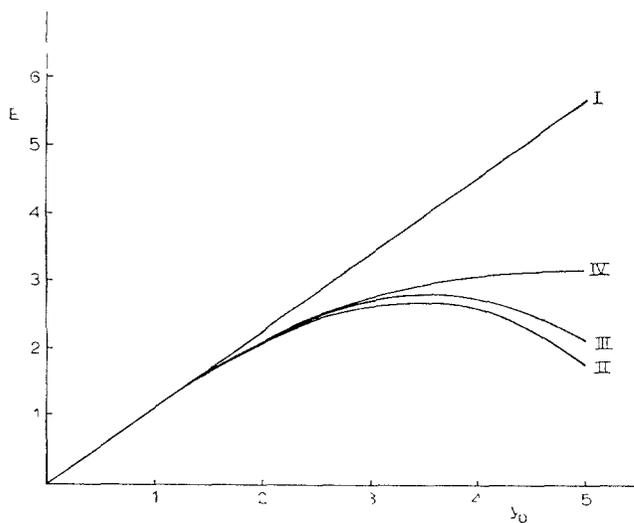
FIG 4 Plot of E as a function of γ for $z_+ = z_- = 1$, $\kappa a = 5$ $m_+ = m_- = 0\,184$ I—Henry Eq (32), II—Overbeek, Eq (33) III—Booth, Eq (35), IV—Wiersema et al, numerical results.

tively confirmed by the results of Wiersema *et al.;* for higher ζ-potentials, the relaxation effect appears to be overestimated by these approximations.

Another conclusion, which follows from further details given by Wiersema *et al.* (32, 35, 36) concerns the electrophoretic retardation. In Section III,A we mentioned that Henry (18) had used the linear equation (8) instead of Eq. (7). The computer results show that, as long as only the electrophoretic retardation is considered, the linearization of Eq. (7) introduces a surprisingly small error. This conclusion also applies to other valence types of electrolytes.
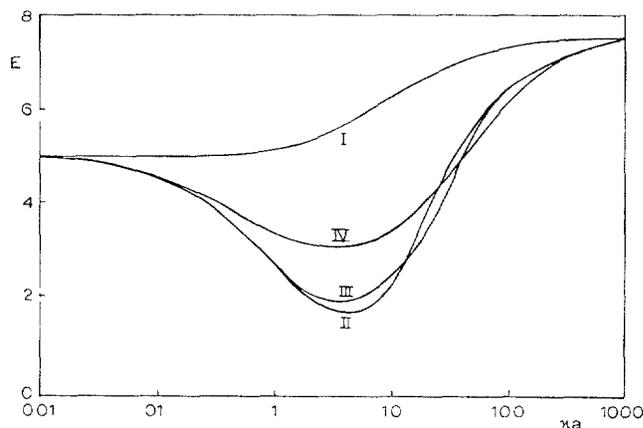
Fig. 5. Plot of E as a function of κa for $z_+ = z_- = 1$, $y_0 = 5$, $m_+ = m_- = 0.184$. I—Henry, Eq. (32); II—Overbeek, Eq. (33); III—Booth, Eq. (35); IV—Wiersema *et al.,* numerical results.

The dependence of E on m_+ and m_- was investigated by means of a few special computations (for univalent electrolytes only). It was found that, as the mobilities, $\lambda_+{}^0$ and $\lambda_-{}^0$ increase, the relaxation effect decreases, with the result that the E.M. increases. For example, at $\kappa a = 5$ and $y_0 = 5$, and for a positive colloid particle, the value of E changes from 3.17 to 3.23 when K^+ is replaced by H^+; for a negative colloid, when K^- or H^- are acting as counterions, the corresponding increase of E is from 3.17 to 3.46. In all circumstances where the relaxation effect is negligible, the E.M. does not depend on $\lambda_+{}^0$ and $\lambda_-{}^0$.

4. *Other Types of Electrolytes*

Additional types of electrolyte considered by Wiersema *et al.* (32, 35, 36) are 2–2, 2–1, 3–1, 1–2, and 1–3. Because of computational problems, the results are limited to rather low values of y_0.

The effect of the valences on the E.M. is pronounced, especially for counterions. Multivalent counterions give a negative relaxation effect, i.e., a decrease of the absolute value of the E.M. For these ions, the absolute value of the relaxation effect increases strongly with increasing valence. For multivalent co-ions, most of the data show a negative relaxation effect which decreases in absolute value with increasing valence; for tri-valent co-ions, the relaxation effect is positive in the region $0.01 < \kappa a < 1$.

5. *Application to Practical Cases*

In the application of the theory, the problem is how to calculate ζ, or the corresponding electrokinetic charge, when the E.M. and certain parameters, such as κa, are given. This problem is extensively discussed in References 35 and 36. We wish to emphasize that the equations given in Section III.A may be good approximations in many cases; these equations should be used whenever possible, because it is always more convenient to work with analytical expressions than with a set of numerical data. We shall now give some details (for 1–1 electrolytes) that may be helpful in estimating the validity of the analytical approximations when the E.M. is known from experiment and the ζ-potential is still unknown. Figure 6, indicating the range of validity of the various treatments, serves as an illustration of the following considerations.

First, one should decide, whether one of the very simple expressions of von Smoluchowski [Eq. (30)], or of Hückel [Eq. (31)] is valid. This can be done by inspection of Fig. 3; when the experimental combi-
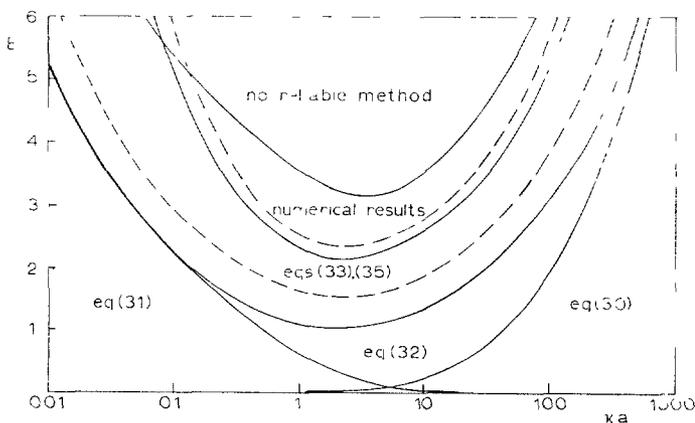
FIG. 6. Range of validity of calculations of the electrophoretic mobility for 1—1 electrolytes. Solid lines correspond to an error of 1 mV in the ζ-potential; dotted lines, to an error of 2.5 mV. For further explanation see text.

nation of E and κa lies within a region where E does not depend on κa, one may use Eq. (30) ($\kappa a \gg 1$) or Eq. (31) ($\kappa a \ll 1$). In Fig. 6, the range of validity of these equations is shown in a different way. For combinations of E and κa which lie inside the region in the lower left-hand corner of this diagram. Eq. (31) will lead to an error of less than 1 mV in the ζ-potential. In this context (and in the following discussion of Fig. 6) an error means a difference between two values of ζ calculated by means of the analytical approximation and by means of the computer results of Wiersema *et al.* (32, 35, 36). [The drawn curve forming the upper boundary of the "Hückel region" is rather schematic; e.g., it does not account for the fact that, for $\kappa a = 10$ and $y_0 = 3$, Eq. (31) *happens* to be exact (cf. Fig. 3), because, for this combination of κa and y_0, the Henry correction and the relaxation correction to Eq. (31) just compensate each other.] The validity of Eq. (30) has been indicated in a similar way, the drawn curve corresponding to an error of 1 mV in ζ.

When it is decided that Eq. (30) or (31) is not sufficient, the next step is to find out whether Henry's equation (32) is valid. This is shown in Fig. 6 in a somewhat more detailed way; when an error of 2.5 mV in ζ can be tolerated, the "Henry region" is extended upward to the lower dotted line. The diagram gives similar information with respect to Overbeek's equation (33) and to Booth's equation (35) for univalent electrolytes. Figure 6 applies to the case $m_+ = m_- = 0.184$ [cf. Eq. (29)], but it is a good approximation for other values of m_+ and m_-.

Detailed instructions for the calculation of ζ from the computer results are given by Wiersema *et al.* (35, 36). The limitations of the computer results for univalent electrolytes are given by the upper drawn line in Fig. 6. If an electrophoresis experiment implies a combination of E and κa (e.g., $E = 4$, $\kappa a = 5$) which lies above this line, it is not possible to calculate the ζ-potential from the computer data. This situation may exist either because the computations were not carried through sufficiently far (i.e., for $y_0 < 6$ only) or because the theoretical curve of E vs y_0 exhibits a maximum (cf. Section III.D,3).

The electrokinetic charge, Q, can be calculated from the ζ-potential. For this purpose, the equation

$$Q = \epsilon \zeta a (1 + \kappa a) \tag{36}$$

is sometimes used. This is, however, a linearized approximation based upon Eq. (8); it is valid only for low values of ζ and κa. More exact numerical relations between Q and ζ, based on the solution of Eq. (7) for a spherical particle, were obtained by Hoskin (33) and by Loeb *et al.* (34). Some preliminary results of the latter authors are given in

Vol.I (1). Reference 34 contains more details, which include the relation between Q and ζ for unsymmetrical electrolytes and a discussion of Eq. (36) and other analytical approximations.

6. *Comparison between Theory and Experiment*

One of the requirements that should be met by a sensible theory is that, at least in principle, it should be possible to prove or disprove it experimentally. With the theory of electrophoresis, this is rather a problem, at least when a complete quantitative test is required. Because the problem is a fundamental one, we shall discuss it here, repeating some arguments given elsewhere (35, 36).

The theory predicts a relation between the electrophoretic mobility and the ζ-potential. Of these two, the E.M. can be measured directly, whereas the ζ-potential (or changes of ζ) cannot.

Following an indirect approach, one may try to correlate E.M. measurements with ζ-potentials obtained from other electrokinetic phenomena, such as electrosmosis and streaming potential. But such values of ζ are always calculated from a theory that has many features in common with the theory of electrophoresis itself. These features (such as the assumption of constant values of ϵ and η in the mobile part of the double layer) escape testing if one follows this approach.

Another method would be the correlation of E.M. measurements with other experiments that provide information concerning the double layer. As examples we mention colloidal stability, electrocapillary phenomena, direct measurements of changes of the surface potential across monolayers, and determinations of the particle charge by titration. But none of these methods leads directly to the ζ-potential or to the electrokinetic charge. Hence, additional theoretical assumptions concerning, for instance, the relation between ψ_0 and ζ, cannot be avoided. Because the theory of the inner region of the double layer is by no means perfect, this type of approach involves the risk of testing too many theories at the same time.

From these arguments it follows that it is not possible to obtain values of ζ that are both quantitatively reliable and completely independent of the theory of electrophoresis. Hence, we must be satisfied with testing the theory in a semiquantitative way. For this purpose, suitable E.M. measurements are needed in the first place, whereas other experiments, such as those mentioned above, can give valuable additional information.

The requirements that should preferably be met by suitable E.M. measurements, are discussed by Wiersema *et al.* (35, 36). For instance, it is important that certain variables, such as κa and ζ, can be changed independently of each other. When κa is changed by varying the ionic

strength, ζ may also change considerably Hence, it is better to work with monodisperse colloidal solutions of different particle sizes

From a survey of the literature Wiersema *et al* (35 36) conclude, that there is a lack of experimental data that can be used to test theoretical predictions This has been emphasized by other authors (4 26, 31) We know of only four investigations (20, 37–40) that were carried out systematically with a view to checking theoretical results for rigid spherical particles Of these, the measurements by Mooney (20) and by Kemp (37) are not suitable to test the more recent theories Mooney's experiments were done with oil droplets, in which internal circulation may have occurred invalidating the assumption of rigidity of the particles In Kemp s experiments the mobilities are so low that hardly any influence of relaxation is expected The work of von Stackelberg and Heindze (38) was done with the purpose of testing the results of Overbeek (24, 25) and of Booth (26 27) The very recent investigation by Shaw and Ottewill (39, 40) on monodisperse polystyrene latices is by far the most systematic and comprehensive one

We shall now review the conclusions that can be drawn from inspection of the experimental work that is now available, more detailed discussions can be found in References 35 and 36

An interesting feature of the computer results is the maximum in the $(E\,y_0)$ curve (e g, for 1–1 electrolytes and $5 < \kappa a < 50$, cf Fig 3) This implies that the E M does not exceed a certain value whatever happens to the ζ-potential Hence, it is of interest to find out whether mobilities have been observed (for appropriate values of κa) that do exceed the predicted maximum A survey of the literature (35 36) shows that such observations are very exceptional The exceptions are data on silver iodide sols published by Troelstra and Kruyt (41, 42) and by Watanabe (43) and especially some results found by Shaw and Ottewill (39, 40) with polystyrene latices The differences between predicted maxima and observed mobilities are small but they do indicate that the theory is somehow incomplete and that in those extreme cases (and, perhaps in other ones as well) the relaxation effect has been slightly overestimated On the other hand, the same literature study (35, 36) shows that the computer results explain more facts than do the approximate equations of Overbeek (24 25) and of Booth (26, 27) In particular a number of cases of high mobilities have been observed by Stigter and Mysels (44) on soap micelles, by Shaw and Ottewill (39, 40) on polymer latices, and by Troelstra and Kruyt (41, 42), Watanabe (43), and Parfitt and Smith (45, 46) on silver iodide sols These mobilities are above the limits predicted by the equations of Overbeek and of Booth but well within the range of the computer data

Another important question is whether the E.M. changes with κa in the predicted way. In this respect, the theory is qualitatively confirmed by a number of measurements, such as those of von Stackelberg and Heindze (38) and especially by the work of Shaw and Ottewill (39, 40). In his recent thesis, Shaw (39) also reports evidence that, qualitatively, the E.M. varies with the mobility of the counterions as predicted by the computer results.

We conclude that the recent theory presented in this section is basically sound, but probably needs some refinement; further, that more systematic experiments seem to be most needed at this stage.

IV. Theories for Other Models

The calculations dealt with in Section III have been based on a model and on certain assumptions listed in Section III,B. In the present section we shall consider to what extent these assumptions restrict the applicability of the theory and what happens to the theory when one or more of these restrictions are removed. Of course, the two aspects are closely connected; in some respects, the second aspect must be dealt with before the first one can be handled. The reader of this section will find that there are still many unsolved theoretical problems.

In the discussion that follows, the list of assumptions given in Section III,B will be adopted as a framework. We have found it convenient to start at the bottom of the list and to proceed upward from there.

A. MIXTURES OF ELECTROLYTES

In many practical cases, mixtures of two or more electrolytes (e.g., from added buffer solutions) are present in the colloidal system. Let us consider to what extent these cases are covered by the theory.

In the theory of Henry (18), the small ions are characterized only by their valences and not by their mobilities. Equations (17) and (19), the limits for large and small κa, respectively, are even completely independent of the nature of the small ions.

For mixtures of univalent electrolytes, Fig. 6 can be consulted in order to find out whether Henry's theory can be used; for mixtures of unsymmetrical electrolytes, this decision must be based upon the data given by Wiersema *et al.* (35, 36). When the electrolytes are of different valence types (e.g., $NaCl + K_2SO_4$), the decision is complicated by the fact that Wiersema *et al.* have not included mixtures of different valence types. In this case it is advisable to let the valence of the most highly

charged counterion decide the issue; e.g., for a positive colloid in NaCl + K_2SO_4, the data for 1–2 electrolytes should be inspected. For a negative colloid in the same electrolyte mixture, the use of Fig. 6 will not cause serious errors.

Once it has been found that Henry's theory can be used, the calculations are straightforward because the ionic valences enter into Henry's result [Eq. (20)] only through the parameter κ [cf. Eq. (9)]. The value of κ is easily calculated even for mixtures of different valence types.

The theory of the relaxation effect gives results in which the ionic valences appear not only indirectly, through κa, but also as separate parameters that have a strong effect on the E.M. These results also depend, in a much less pronounced way, on the mobilities of the small ions.

For mixtures of univalent electrolytes, the theory of the relaxation effect can be applied (35, 36) without appreciable errors by taking number averages of the ionic mobilities, or of the parameters m_+ and m_- [cf. Eq. (29)]. For mixtures of unsymmetrical electrolytes of the same valence type, one can take similar number averages and account for these average mobilities by means of an approximate method suggested by Wiersema *et al.* (35, 36). Measurements of the E.M. in electrolyte mixtures of different valence types are difficult to interpret when the relaxation effect cannot be neglected; for this case no calculations are available and no reliable approximate method can be suggested.

In the calculation of the electrokinetic charge, Q, from the ζ-potential, mixtures of electrolytes cause no problem as long as the Debye-Hückel approximation, Eq. (36), is valid. This can be decided by consulting the work of Loeb *et al.* (34); for mixtures of the same valence type, the decision is straightforward and for mixtures of different valence type, the data for the most highly charged counterion should be inspected. When Eq. (36) is not valid (high ζ and/or high κa), Q can be calculated from ζ by means of the tables of Loeb *et al.* (34) as long as the electrolyte solution does not contain different valence types; for mixtures of different valence types, no exact data are available.

B. The Gouy-Chapman Theory

The Gouy-Chapman theory is open to a considerable number of criticisms. Briefly stated, the Poisson-Boltzmann equation (7) contains a fundamental inconsistency; the dielectric constant decreases in the direction toward the particle; the small ions do have a finite volume and are often specifically adsorbed on the particle surface; the surface charge is not continuous but discrete. A corresponding number of corrections to the Gouy-Chapman theory have been proposed. They have been reviewed in

Vol. I (1) and, more recently, by Haydon (6). The question here is how these corrections affect the theory of electrophoresis.

We shall first consider the relation between the E.M. and the ζ-potential; the relation between ζ and the electrokinetic charge will be discussed at the end of this section.

The fundamental *inconsistency,* inherent in the use of the *complete Poisson-Boltzmann equation* (7), was first pointed out by Fowler (47); further references can be found in Vol. I (1). The objection is that the exponential terms in Eq. (7) contain the average potential, ψ, instead of the potential of the average force acting on an ion in the vicinity of the colloid particle. In other words, when a small ion is brought from infinity to a certain position in the double layer, the amount of work done must be corrected, because the ion creates its own "atmosphere" at that position. For a colloidal double layer in equilibrium (no external field) this "self-atmosphere effect" was calculated by, among others, Loeb (48) and Levine and Bell (49).

Centering the discussion on electrophoresis, we first observe that Eq. (17) (von Smoluchowski) and Eq. (19) (Hückel) are not based on any specific potential distribution and are, therefore, not affected by Fowler's criticism. Furthermore, Onsager (50) has pointed out that in the linear equation (8) the use of the average potential, ψ, is theoretically consistent. For this reason, the electrophoresis theory of Henry (18), which is based on Eq. (8), is not open to the objection discussed here. Hence, complications can be expected only as far as the theory of the relaxation effect is concerned. In this theory it is assumed that Eq. (7) is valid in the absence of an external field. Casimir (51) has shown that the inconsistency in Eq. (7) is not serious when this equation is used to describe the potential distribution around a single, highly charged, colloid particle as long as the concentration of ordinary electrolyte ions is small. This conclusion is supported by Levine and Bell (49) who consider the self-atmosphere effect as one of the less important corrections to the Poisson-Boltzmann equation for a plane double layer. In the theory of the relaxation effect, another complication arises from the fact that the small ions, as they move in the external field, are retarded by their own atmospheres. This additional self-atmosphere effect is ignored by using the limiting equivalent conductances, $\lambda_+{}''$ and $\lambda_-{}''$, in Eq. (29). However, from an approximate calculation by Wiersema (35) it follows that this effect is negligible in most practical cases and that it is, in addition, to a large extent canceled by the Brownian motion correction (cf. Section IV,H). Recently, the conductivity of strong electrolytes has been treated (52, 53) by advanced statistical mechanical methods that avoid the inconsistency connected with Eq. (7). This type of approach has not yet been applied

to colloids We conclude that, although no reliable quantitative conclusions are available beyond the Henry region the complications discussed above can probably be neglected without appreciable error

The *dielectric constant* in the double layer ϵ, decreases in the direction toward the particle for two reasons In the first place the molecules of the liquid are oriented by the electric field caused by the particle charge (dielectric saturation) Second the charges of the small ions in the double layer have a similar effect on the dielectric constant, this effect which is small compared to the first one, increases in the direction toward the particle, because the total ionic concentration increases in that direction Several authors have corrected the Gouy-Chapman theory for these effects Since their work has been reviewed rather extensively by Haydon (6), we shall give only a few conclusions here

We recall that in the treatment by von Smoluchowski (cf Section III, A), the assumption that ϵ and η are constants is implicit in the derivation of Eq (17) A more general expression is

$$\frac{U}{X} = \frac{1}{4\pi} \int_{\zeta}^{\zeta} \frac{\epsilon}{\eta} \, d\psi \qquad (37)$$

It follows that other things being equal a decrease of ϵ gives a smaller mobility, for similar reasons the E M is overestimated by all other theories discussed in Section III

Lijklema and Overbeek (14) have considered the effect of dielectric saturation using an equation obtained by Booth (54) The results are given in Table I From these data it follows that the correction to the dielectric constant is important only for combinations of high electric potential and high ionic concentration This conclusion is in agreement with an estimate given by Levine and Bell (49) The over-all correction to the E M [obtained by carrying out the integration in Eq (37) (considering η to be a constant) and comparing the result with Eq (17)] is even smaller because the integral includes those regions of the double layer in which dielectric saturation is practically negligible, e g , for a concentration of 1×10^{-4} N and for $\psi = 270$ mV, the correction to ϵ is 10%, but for the same concentration and $\zeta = 270$ mV, the correction to the E M is only 1% As a high electrolyte concentration depresses the ζ-potential, the limits given in Table I will not easily be reached, although for the high concentrations this is not impossible

The above discussion concerns the primary effect which is already present even when only Poisson's equation (13) is involved The theory of Henry and the theories of the relaxation effect (25, 27, 36) are subject to additional corrections because they are also based on a specific po-

TABLE I

EFFECT OF DIELECTRIC SATURATION ON ELECTROPHORETIC MOBILITY[a]

Molar concentration of univalent electrolytes	Dielectric saturation of		Total correction on E.M. of 1%
	10%	1%	
1	40	15	25
10^{-1}	94	40	67
10^{-2}	148	94	131
10^{-3}	210	148	201
10^{-4}	270	210	268

[a] The second and third column give the values of the diffuse double layer potential, ψ, above which the dielectric saturation exceeds 10% and 1%, respectively. The last column gives the values of the electrokinetic potential, ζ, at which the dielectric saturation correction to the E.M. exceeds 1%. Calculations are based on Eq. (37) with constant value of η. (This table is an extended version of Table I occurring in Reference 14; the values of the potential given in the second column of the latter table correspond to a saturation of 1%, not 2%.) Values of ψ and ζ are expressed in millivolts.

tential distribution calculated with the assumption of a constant ϵ. However, as was discussed in Section III,D,3, the treatment of electrophoretic retardation, according to Henry (18), is very insensitive to the potential distribution that is used. The dielectric constant also occurs in the higher terms in ζ [cf. Eq. (21)] that appear when the relaxation effect is considered. But accounting for dielectric saturation in those terms would have only a very minor effect on the E.M. (a correction to a correction). Hence it is safe to conclude that these secondary effects are negligible.

The *finite volume* and the *specific adsorption* of the electrolyte ions were first considered by Stern (55), whose theory was refined by Grahame (56) and other workers [cf. Vol. I (1) and Haydon's review article (6)].

The *finite volume* of the ions gives a relatively large correction to the Poisson-Boltzmann equation. However, this correction does not affect Eqs. (17) and (19) because no specific potential distribution needs to be assumed in the derivation of these equations. The same applies to Henry's result [Eq. (20)] because this result is based upon the linearized Poisson-Boltzmann equation and because Henry's treatment is not sensitive to the potential distribution that is used (cf. Section III,D,3). Hence, only the relaxation theory is affected by the volume correction. For a flat double layer in equilibrium, Levine and Bell (49) conclude that the volume correction to the potential amounts to 10 to 20% at a surface potential of 100 mV and a 1–1 electrolyte concentration of 0.01 N. We observe that,

at this concentration, a ζ-potential of 100 mV is unlikely to occur. Furthermore, the theory of the relaxation effect is based upon integrations which include the outer regions of the double layer, where the volume effect is negligible; this tends to diminish the overall correction, as in the case of dielectric saturation. On the other hand, for a transport phenomenon such as electrophoresis, the volume effect may cause additional complications, which have not been calculated for colloids. We conclude that the volume effect can be neglected in most cases, except, possibly, for combinations of high ζ-potential and high electrolyte concentrations.

It is generally accepted that most, if not all, the *specific adsorption* occurs within the surface of shear. For this reason, the relation between the E.M. and ζ is not affected by specific adsorption, although this adsorption may have a profound effect on the value of ζ itself.

Recently, *the discreteness of the surface charge* has received considerable attention; we mention here the papers by Levine and Bell (57), Krylov and Levich (58), and Buff and Stillinger (59), where other references can be found. In the electrophoresis theory discussed in Section III, the surface charge, σ, is defined formally by putting

$$\tfrac{4}{3}\pi a^2 \sigma = Q \tag{38}$$

where Q is the electrokinetic charge and a is the distance between the center of the particle and the surface of shear; σ is then assumed continuous. When this continuous distribution is replaced by a discrete one, the ionic distribution outside the surface of shear may also change. Referring to the discussion of Section II (cf. Fig. 1), we observe that both k_1 and k_2 are independent of the way in which the particle charge and the atmospheric countercharge are distributed. The electrophoretic force, k_3, is calculated from the distribution of the countercharge and, therefore, depends indirectly on the structure of the particle charge. The relaxation force, k_4, is obtained by adding (integrating) all Coulomb forces between the charge Q and the distorted ionic atmosphere. Hence, the latter force depends on the distributions of both Q and the atmospheric charge.

However, the discreteness of charge effect is a short-range effect which is mostly confined to the inner regions of the double layer. It is, therefore, not unreasonable to assume that the surface of shear remains a surface of constant potential and to use the Poisson-Boltzmann equation in the region outside that surface. As a consequence, in many cases the forces k_3 and k_4 (and hence, the relation between ζ and the E.M.) will not be affected much by the discreteness of the particle charge. The discreteness becomes important when relatively few elementary charges per particle are present and when the electrolyte concentration is high. In that case, separate ionic atmospheres are formed around the charged sites, and the

concept of ζ-potential breaks down, with the result that the Gouy-Chapman model becomes rather unrealistic.

From the preceding discussion we conclude that the effect of the various corrections is, generally speaking, rather small as far as the relation between ζ and the E.M. is concerned. The most important reason is that, in the derivation of this relation, one uses only the mobile part of the double layer, including regions where the corrections are negligible. Yet it is quite possible that the use of the uncorrected Poisson-Boltzmann equation in the calculations of Wiersema *et al.* (32, 35, 36) has caused the small discrepancies between these calculations and certain experiments (cf. Section III,D,5).

We conclude this section with a few remarks on the relation between electrokinetic charge and ζ-potential. This relation is based on

$$\sigma = -\frac{\epsilon}{4\pi} \, \text{grad} \, \psi \qquad (39)$$

where σ is defined by Eq. (38). In Vol. I (1), Eq. (39) has been worked out for a few specific cases; e.g., for a spherical particle, grad $\psi = d\psi/dr$, where r is the distance from the center of the sphere; when $d\psi/dr$ is calculated from the linearized Poisson-Boltzmann equation (8), one obtains Eq. (36) of this chapter. Here we emphasize that, in the right-hand side of Eq. (39), the values of ϵ and grad ψ *at the surface of shear* are to be substituted. At this surface the various corrections to the Gouy-Chapman model have the highest values attainable in the mobile part of the double layer. Furthermore, we observe that, in order to work out Eq. (39) it is always necessary to assume a specific potential distribution, whereas some of the simpler relations between ζ and the E.M. are based only on Poisson's equation. It follows that, as far as the Gouy-Chapman model is concerned, the calculation of Q from ζ compares unfavorably with that of ζ from the E.M., even when the exact results of Loeb *et al.* (34) are used. The effect of the corrections on the relation between charge and potential has been recently discussed by Haydon (6) and by Devanathan and Tilak (60). To a certain extent, the corrections compensate each other. Hence, it is not advisable to apply one or two corrections and to leave out others. As the refinements of the double-layer theory are still subject to much discussion, we suggest the use of the Gouy-Chapman results in cases where accuracy is not too important.

C. THE VISCOELECTRIC EFFECT

As has been mentioned in Section II, it is usually assumed in theories of electrophoresis that one or a few molecular layers of liquid adjacent

to the particle are completely immobilized and that they are separated by a sharp "surface of shear" from liquid with unchanged viscosity. Presumably the transition from "infinite" viscosity to normal viscosity is not quite as sharp as that, but so long as the mechanism that immobilizes the liquid molecules is not specified, further progress is not possible. Lijklema and Overbeek (14) have suggested that the strong electric field in the double layer may be the cause of the increased viscosity. As a matter of fact, according to Andrade and Dodd (61) the viscosity of a liquid is increased in an electric field according to

$$\eta = \eta_0 [1 + f(d\psi/dx)^2] \tag{40}$$

In Eq. (40), $d\psi/dx$ is the electric field strength, η and η_0 are the viscosities in the field and without electric field, respectively, and f is the "viscoelectric constant," which for a few organic liquids is of the order of 10^{-12} cm^2 volt^{-2}. The viscoelectric constant of water has not been measured but on the basis of a theoretical argumentation, Lÿklema and Overbeek (14) suggested it to be of the order of 10^{-11}cm^2 volt^{-2}.

Substituting the viscosity as a variable according to Eq. (40) into Eq. (37) and carrying out the integration (with ϵ constant), Lÿklema and Overbeek found that the viscoelectric effect may have a strong influence on the E.M. and may immobilize quite a substantial layer of liquid around the particle; the thickness of this layer varies with the electrolyte content and with the charge of the particle.

However, more recently experimental evidence has been presented by Hunter and Alexander (62) and by Stigter (63), indicating that the viscoelectric effect for water may have been strongly overestimated. In particular, Stigter's work on the viscosity and self-diffusion in solutions containing micelles of sodium lauryl sulfate indicates that the surface of shear coincides within 1 Å with the surface enveloping the hydrated (one layer of water molecules) heads of the micellized ions, whereas the estimate of Overbeek and Lijklema would lead to an immobilized layer of 9 Å.

In this situation the most practical approach is not to take the viscoelectric effect into account. But it is obviously desirable to measure the viscoelectric constant for aqueous solutions and to obtain further evidence concerning the position of the surface of shear.

D. Conducting Particles and Surface Conductivity

The influence of the bulk electric conductivity of the colloid particle on the E.M. was calculated by Henry (18) for spherical and cylindrical particles without accounting for the relaxation effect. Henry's conclusions have been reviewed rather extensively in References 4 and 7. When both

the particle and the surrounding liquid are electric conductors, the shape of the electric field in the double layer (and hence, the electrophoretic retardation) depends on the conductivities of particle and liquid. In particular, when the two conductivities are equal, the lines of force in the double layer run straight from anode to cathode. In this case, and for a spherical particle, Eq. (19) of Hückel (15) is obtained for any value of κa. When the particle is a much better conductor than is the liquid, the electric field in the double layer is deformed, but the effect of this deformation depends on κa. For the latter case, Henry (18) calculated that the E.M. of a spherical particle follows Hückel's equation (19) in the region $\kappa a < 0.5$ and then decreases with increasing value of κa, reaching zero for $\kappa a = 1000$. The mathematical difficulties which arise if one wishes to consider both the relaxation effect and the conductivity of the particle, were pointed out briefly by Overbeek (24, 25), but this problem has not been worked out.

Fortunately, there is a strong theoretical argument (24, 25), supported by experimental evidence, showing that in electrophoresis even metallic particles can be treated as insulators. Any flow of electricity through the bulk of a conducting particle would require electrolytic reactions at the boundary of the particle. From ordinary electrolysis experiments it is known that such reactions do not occur unless the imposed potential difference between solid and liquid exceeds a certain value (the polarization tension) which is of the order of several millivolts. In normal electrophoresis experiments, the external field strength does not exceed 10 volts/cm. In a field of this strength there would be a potential difference of only 1 mV across a particle having a diameter of 1 μ. It follows that in most practical cases the polarization will be sufficient to prevent flow of electricity through a conducting colloid particle. This conclusion is confirmed by experiments of Bull and Söllner (64) on mercury emulsions. These authors found an E.M. of 3×10^{-1} cm^2/volt-second in the region $10 < \kappa a < 100$; if the mercury droplets followed Henry's theory for conducting particles, the E.M. would certainly be much lower. Henry (18) quotes one experiment in which the E.M. was found to be zero, but this concerns a relatively large object (a fine silver fiber at which the polarization tension was deliberately kept low). We conclude that, as long as there is no experimental evidence that colloid particles consisting of conducting material really behave as conductors, the theory for insulating particles should be applied in these cases.

The concept of surface conductance is discussed by Davies and Rideal (65). The effect of surface conductance on the E.M. has been treated by Booth (66) and by Henry (67). The physical assumptions of the two authors are rather different. According to Booth (66) the surface region

of the particle itself may have a high conductivity. Henry (67) attributes
the surface conductance to the excess of ions in the double layer. The
mathematical methods and the results of the two authors are similar;
they both find that surface conductance may depress the E.M. consid-
erably. However, in order to avoid confusion it is necessary to observe
that the conductance arising from the region outside the surface of
shear is implicitly accounted for in the treatments of the relaxation effect
by Overbeek (24, 25), by Booth (26, 27), and by Wiersema *et al.* (32,
35, 36). This is so because the use of local, not bulk concentrations in the
first term of the transport equation (24) implies that the ionic conductiv-
ity in the double layer differs from the bulk conductivity. In other words,
as far as the region outside the surface of shear is concerned, surface
conductance and relaxation effect are two concepts describing the same
phenomenon (7). Up to the present, the latter concept has yielded the
more complete theory; in the treatments by Booth (66) and Henry (67),
interaction between surface conductance and electrophoretic retardation
is neglected and in the results of these calculations the surface conductance
appears as a parameter that is still to be determined. Hence, generally
speaking, no surface conductance correction should be applied when the
relaxation correction can be calculated or when the latter correction has
been found negligible (e.g., for spherical particles and $\kappa a \ll 1$ or
$\kappa a \gg 1$).

The latter conclusion would not be valid if there were an appreciable
surface conductance arising from the region inside the surface of shear.
As it is improbable that electrons act as charge carriers (see above),
the only remaining mechanism for such a surface conductance is the
movement of adsorbed ions in the inner region of the double layer. In
order to give a contribution to the E.M., these ions would have to mi-
grate across the surface of shear, entering the inner region at one side
of the particle and leaving this region at the other side. Such a mechanism
is not accounted for in the theories of the relaxation effect (25, 27, 36)
since in these theories one of the boundary conditions excludes transport
of ions across the surface of shear. There remains the question whether
this mechanism indeed occurs. Measurement of the surface conductance
is possible (65) but does not distinguish between different types of con-
ductance. In principle, this difficulty could be solved by means of calcula-
tion. The surface conductance arising from the excess ionic concentration
in the diffuse part of the double layer has been calculated by Bikerman
(68) and by Hesselink and Van der Waarde (69). (These calculations
apply to flat double layers and the value of ζ must be known in order
to obtain quantitative conclusions from this work.) From the above con-
siderations it follows that, only if the experimental value of the surface

conductance significantly exceeds the value calculated from excess ionic concentrations in the diffuse region, one may conclude that a contribution from the inner region is present. Only in that case it would be advisable to apply, in addition to the relaxation correction, a correction according to Booth (66) or Henry (67), substituting only the surface conductance arising from the inner region into the equations of these authors.

E. DIELECTRIC CONSTANT OF THE PARTICLE

In all theories (3, 15, 18) neglecting the relaxation effect, the dielectric constant, ϵ_i, of the colloid particle does not occur in the basic equations. In the theories of Overbeek (24, 25), of Booth (26, 27), and of Wiersema et al. (32, 35, 36), ϵ_i appears in one of the boundary conditions which determine the electric potential, Λ, in the distorted ionic atmosphere. Accordingly, the expression for Λ contains a term that depends on ϵ_i, but Wiersema et al. (32, 35) have shown analytically that this term does not give a contribution to the E.M.; this result confirms the conclusions of Overbeek (25) and of Booth (27). Hence, all theories predict that the E.M. does not depend on the dielectric constant of the particle. Up to the present, no experimental evidence contradicting this conclusion has been found.

F. NONRIGID PARTICLES

This section deals with spherical particles having a finite viscosity, such as emulsion droplets and air bubbles. In this case one must consider the possibility of motion of the fluid within the particle. When this motion occurs, the velocity pattern in the surrounding solution is affected; in particular, the tangential component of this velocity does not vanish at the interface as it does in the case of a solid particle. As a result, the Stokes friction will be diminished; the electrophoretic retardation and the relaxation effect will also be different.

The only detailed theoretical analysis of this problem was given by Booth (70). Omitting the relaxation effect, he calculated the E.M. of a fluid sphere of arbitrary electrical conductivity for arbitrary values of κa, and for the following three cases: (a) no electric charge within the sphere (the whole charge is concentrated at the interface); (b) uniform distribution of charge throughout the sphere; (c) ionic double layer in the sphere. Of the rather complicated results, only a few limiting cases *for nonconducting particles* will be reviewed here. For this purpose we represent the electrophoretic mobility by

$$\frac{U}{X} = \frac{\epsilon \zeta}{6\pi\eta} G\left(\kappa a, \eta, \eta'\right) \tag{41}$$

where the effect of the finite viscosity, η', of the particle is included in the function G. In case (a) (no charge in the sphere) Booth finds that, for $\kappa a \ll 1$, $G = (6\eta' - 3\eta)/(6\eta' + 4\eta)$ and, for $\kappa a \gg 1$, $G = 9\eta'/(6\eta' + 4\eta)$. With these values of G, and for $\eta' \gg \eta$ (solid particle), Eq. (41) is reduced to Hückel's equation (19) ($\kappa a \ll 1$) or to von Smoluchowski's equation (17) ($\kappa a \gg 1$). These results further imply that internal motion depresses the E.M. and even that, for $\kappa a \gg 1$ and $\eta' = 0$, the E.M. vanishes. As Booth himself observes, this is not consistent with the fact that air bubbles show electrophoresis. For case (b) (uniform charge in the sphere) and $\kappa a \ll 1$, the function G in Eq. (41) was found to equal $(3\eta' + 3\eta)/(3\eta' + 2\eta)$ (giving a positive correction to the Hückel equation); for case (b) and $\kappa a \gg 1$, Booth's equation does not give a finite limiting value for the E.M. For case (c) (ionic double layer in the particle), Booth's result depends, in addition, on the thickness of this double layer; when the inner double layer is relatively thick, the result is reduced to that of case (b).

The internal circulation correction was also discussed by Jordan and Taylor (71) for the case in which no charge is present within the sphere. Their calculation is based on the fact that, because of internal motion, the Stokes friction is decreased (72) by a factor of $(3\eta' + 2\eta)/(3\eta' + 3\eta)$. Assuming that the E.M. is increased by the reciprocal of this factor, Jordan and Taylor obtain, for a nonconducting particle,

$$\frac{U}{X} = \frac{\epsilon\zeta}{6\pi\eta} \frac{3\eta' + 3\eta}{3\eta' + 2\eta} f_1(\kappa a) \tag{42}$$

where $f_1(\kappa a)$ is Henry's function as given in our notation [cf. Eq. (20) and the discussion following that equation]. Equation (42), giving a positive correction to the E.M., contradicts Booth's result for case (a). We observe that Jordan and Taylor's result does not account for the influence of internal motion on the electrophoretic retardation and on the relaxation effect.

It follows that the theoretical work on this subject is rather unsatisfactory. Turning to experimental evidence, we mention that Taylor and Wood (73), on the basis of E.M. measurements on droplets of different viscosities, decide in favor of Eq. (42). However, other experiments strongly suggest that in many cases internal circulation does not occur at all. Linton and Sutherland (74) studied macroscopic drops (diameters of several millimeters) of various organic substances rising or falling in water. By means of direct observation of the drops they found that internal circulation can be prevented by the presence of very small amounts of interfacially active impurities and that the effect of these impurities

increases with increasing interfacial tension between the two pure liquids and with decreasing size of the drops. (Their explanation is that transfer of momentum across the interface is opposed by differences in surface pressure that are produced when surface-active material is present.) From these experiments one would predict that a small emulsion droplet consisting of a nonpolar substance (high interfacial tension) and stabilized by a surfactant, behaves as a solid sphere. This is confirmed by experiments of Anderson (75), who measured the E.M. of *n*-octadecane dispersions in solutions of sodium dodecyl sulfate at a series of temperatures above and below the melting point of the octadecane. This author found that any correction for internal motion above the melting point would be inconsistent with his observations, which also included measurement of the adsorption of the surfactant as a function of temperature. Recently, Hollingshead *et al.* (76) found that the E.M. of octadecanol droplets is strongly dependent on the purity of the materials and the way of preparation of the electrophoresis cell. These authors also review E.M. measurements on similar systems by previous workers and suggest that discrepancies between the results may be caused by impurities. One might conclude here that the discrepancies are related to variations in the extent of internal circulation. However, acording to Hollingshead *et al.* the materials used in previous measurements had probably been so impure that internal motion had been practically absent.

In our opinion the situation could be clarified a great deal by further experiments, similar to those quoted above. In the meantime, the best approach is to treat fluid drops as solid spheres in cases where the experiments of Linton and Sutherland (74) suggest that internal motion is absent. This certainly includes many important systems, such as oil in water emulsions stabilized by surfactants and oil droplets covered by proteins or other materials of biological interest.

The above discussion applies to nonconducting particles. Fluid spheres consisting of electrically conducting material (e.g., mercury droplets) exhibit a rather extraordinary phenomenon that was discussed by Frumkin (77). This author has shown theoretically that when a conducting droplet in water is subjected to an external dc field, internal circulation occurs. The main cause of this motion is not transfer of momentum across the interface, but consists of electrical forces acting in different directions in different parts of the drop. These forces are present when the particle is polarized (cf. Section IV,D). As a result of the internal circulation the particle is propagated with a velocity that may exceed the normal electrophoretic velocity by several orders of magnitude. Such velocities have, indeed, been observed (77).

G. Nonspherical Particles

This subject is of interest because many colloidal particles do not have a spherical shape. Obviously, any other particle shape makes the calculation of the electrophoretic retardation and of the relaxation effect more complicated. In addition, the electrophoretic velocity of a nonspherical particle depends, generally speaking, on the orientation of the particle with respect to the direction of the external dc field. Hence it is not surprising that the theory for these particles is very incomplete.

A notable exception occurs when the particle is insulating (cf. Section IV,D) and when the thickness, $1/\kappa$, of the electric double layer is small compared with the radius of curvature of any point of the particle surface. For this case, the calculation of von Smoluchowski (3) is valid irrespective of the form of the particle (cf. Section III,A). Furthermore, Overbeek (30) has shown that, for any particle shape, the relaxation effect can be neglected when the double layer is thin compared to any radius of curvature. Hence, in this limiting case, von Smoluchowski's equation (17) can be applied to all particle shapes, and the E.M. does not depend on the orientation of the particle.

Henry (18) has calculated the E.M. of a circular cylinder of infinite length, without considering the relaxation effect. For a cylinder aligned parallel to the external field, he found that Eq. (17) is valid for arbitrary values of κb, where b is the radius of the cylinder, and for arbitrary conductivity of the cylinder. For a nonconducting cylinder with its axis perpendicular to the field, Henry obtained the relation

$$\frac{U}{X} = \frac{\epsilon\zeta}{\pi\eta F'(\kappa b)} \tag{43}$$

In the limit $\kappa b \gg 1$, $F(\kappa b) = 4$ and Eq. (43) is reduced to Eq. (17). For $\kappa b \ll 1$, $F(\kappa b) = 8$ and

$$\frac{U}{X} = \frac{\epsilon\zeta}{8\pi\eta} \tag{44}$$

For intermediate values of κb, the function $F(\kappa b)$ was evaluated graphically from Henry's result by Abramson *et al.* (78), who used the solution of the linear Poisson-Boltzmann equation (8) for cylindrical symmetry. The results have been reviewed by Abramson *et al.* (79) and by Overbeek (4). Some values of $F(\kappa b)$ are given in Table II.

For the application of these results to practical cases (rod-like particles), the orientation of the particles must be considered. If, under the conditions of electrophoresis, there would be an appreciable preference for a special orientation (because of electric dipole moments of the particles

TABLE II

ELECTROPHORETIC MOBILITY OF RANDOMLY ORIENTED CYLINDERS

κb	$F(\kappa b)$	B[Eq. (46)]	B[Eq. (47)]	$6 f_1(2.47 \kappa b)$
0.00	8.00	6.67	6.00	6.00
0.10	7.73	6.49	5.90	5.84
1.00	7.36	6.24	5.75	5.55
1.10	6.87	5.91	5.54	5.37
2.00	6.51	5.67	5.38	5.16
2.40	6.34	5.56	5.31	5.06
3.00	6.10	5.40	5.19	4.95
∞	4.00	4.00	4.00	4.00

or for hydrodynamic reasons), the extent of this orientation would increase with the strength, **X**, of the external field. In that case, the electrophoretic mobility, **U/X,** would depend on **X.** Because, at the moderate field strengths used in electrophoresis, this is not observed, it is safe to assume that the particles are randomly oriented. Abramson *et al.* (79) accounted for this random distribution in an approximate way by assuming that one-third of the particles are oriented along the direction of the field and two-thirds along directions perpendicular to the field. Their result can be expressed as

$$\frac{U}{X} = \frac{\epsilon \zeta}{B \pi \eta} \tag{45}$$

where

$$B = {}^1\!\!/_3[4 + 2F(\kappa b)] \tag{46}$$

This method of calculating the function B (i.e., by averaging reciprocal mobilities rather than mobilities) seems somewhat arbitrary. By taking weighted averages of the mobilities themselves, according to Eq. (47)

$$\frac{1}{B} = \frac{1}{3}\left[\frac{1}{4} + \frac{2}{F(\kappa b)}\right] \tag{47}$$

we obtain different results, but the relative difference does not exceed 12%, as can be seen by comparing the third and fourth columns of Table II.

It is of interest to compare the above results with Henry's equation (20) for a spherical particle. As an example, let us consider a cylinder of finite length l, taking $l = 20b$. The volume of this cylinder is $20\pi b^3$. The radius, a, of a sphere having the same volume equals $2.47b$. From inspection of Eqs. (20) and (45) it follows that the function $B(\kappa b)$ [Eq. (46) or (47)] should be compared with the function $6/f_1(\kappa a)$,

the relation between the arguments of B and f_1 being $\kappa a = 2.47\kappa b$.
Values of the function $6/f_1(2.47\kappa b)$ are given in the last column of
Table II. It follows that, according to Eqs. (20) and (45) to (47), the
difference between the E.M. of a randomly oriented cylinder and that
of a sphere *of equal volume* is rather small, especially when Eq. (47)
is used. This leads to the tentative conclusion that, as long as the relaxa-
tion effect can be neglected, deviations from the spherical shape have
little influence on the relation between the E.M. and ζ.

For particle shapes other than spheres or cylinders, no specific calcula-
tions of the E.M. have been carried out. Furthermore, the relaxation ef-
fect has not been calculated for nonspherical particles, except for an ap-
proximate treatment of polyelectrolyte coils (cf. Section V,C). However,
as mentioned above, the relaxation effect is negligible for relatively thin
double layers of any shape. Generalizing the conclusions for spherical
particles, we may further assume that the relaxation effect can be neg-
lected when the dimensions of the particle are small with respect to $1/\kappa$
(for arbitrary values of ζ) and when $z_-\zeta < 50$ mV (for arbitrary values
of κ; z_- is the valence of the counterions).

For a cylindrical particle, the relation between the electrokinetic
charge, Q, and ζ has been calculated by Abramson *et al.* (78, 79) and
by Dube (80). In our notation, the result can be expressed as

$$Q = \tfrac{1}{2}\epsilon\zeta l[\kappa b \, K_1(\kappa b)/K_2(\kappa b)] \qquad (48)$$

Equation (48) applies when $l \gg b$ and the charge on the ends of the
cylinder is neglected; $K_1(\kappa b)$ and $K_2(\kappa b)$ are Bessel functions of κb;
a few values of these functions are tabulated by Abramson *et al.* (79).
It is based on the linear Poisson-Boltzmann equation (8) and is, there-
fore, valid only for $e\zeta/kT \ll 1$; furthermore, by analogy with the spherical
case (cf. Reference 34), it can be expected to give the best results when
κb is small.

For $\kappa b \gg 1$, and, more generally, for particles of any shape sur-
rounded by a relatively thin double layer, the charge can be calculated
from the solution of the complete Poisson-Boltzmann equation (7) for a
flat surface (1). For a sphere of radius a, Loeb *et al.* (34) found that
the relative difference between values of Q calculated from the exact
(spherical) solution and from the flat plate approximation is about 5%
for $\kappa a = 20$ and $e\zeta/kT = 1$; at constant κa, this difference was found to
decrease with increasing ζ-potential. Generalizing this result to nonspher-
ical particles we conclude that the flat plate approximation will be a rea-
sonable one when $1/\kappa$ does not exceed $1/20$ of the radius of curvature
of the surface.

For a rigid cylindrical particle in a solution containing only its counter-

ions, the complete Poisson-Boltzmann equation (6) can be solved an-alytically. Results are given by Alfrey *et al.* (81) and by Fuoss *et al.* (82).

H. BROWNIAN MOVEMENT

It is a well-known fact that, in electrophoresis, the motion of the col-loid particle in the direction of the dc field is superimposed on its Brown-ian movement. In E.M. measurements, the effect of this random motion is eliminated either by taking averages over a large number of measure-ments (microscope electrophoresis) or because the combined movements of a large number of particles are observed (moving boundary methods). Since all theoretical equations give the superimposed velocity caused by the field, they are directly related to the observed E.M. In this connection, Brownian movement offers no problem.

However in the theory one must consider the fact that the colloid par-ticle, by its Brownian motion, takes part in the relaxation of its ionic at-mosphere. This diminishes the relaxation effect and gives a positive cor-rection to the E.M. This correction is included in the theory of electrolytic conductance (83, 84) but not in the electrophoresis equations given in this chapter. It can be disregarded whenever the relaxation effect is negli-gible.

For a spherical particle in a 1–1 electrolyte, an approximate computa-tion of the upper limit of the Brownian motion correction was carried out by Wiersema (35). The results were reviewed by Wiersema *et al.* (36) and can be expressed

$$0 < \Delta E' < + \alpha y_0^3 (f_\pm)/(f_\pm + f_c) \tag{49}$$

In this equation, $\Delta E'$ is the Brownian motion correction to the E.M., expressed in dimensionless units [cf. Eq. (27)]; $y_0 = e\zeta/kT$; $f_\pm$ are the friction coefficients (assumed to be equal to each other) of the small ions, and f_c is the friction coefficient of the particle; α is a function of κa, of which the following values are known: $\kappa a = 0$, $\alpha = 0$; $\kappa a = 0.1$, $\alpha = 0.004$; $\kappa a = 1$, $\alpha = 0.018$; $\kappa a = 5$, $\alpha = 0.030$. We observe that a large value of κa implies either a large particle radius or a large ionic strength. In the first case, $f_\pm/(f_\pm + f_c)$ is small; in the latter case, it is unlikely that y_0 has a large value. It follows that the Brownian motion cor-rection is negligible in most practical cases. Moreover it was found (35) that $\Delta E'$ is canceled to a large extent by the self-atmosphere effect (cf. Section IV,B) which slightly diminishes the mobility of the small ions, and, hence, that of the particle. Therefore, and because Wiersema's calcu-lation gives only the upper limit of $\Delta E'$, the best one can do at present is to

neglect the Brownian motion correction as well as the self-atmosphere effect.

I. Effect of Nonlinear Terms

In the theory presented in Section III, two approximations have been made that will be briefly discussed here. First, the Navier-Stokes equation (25), given in Section III,C is, strictly speaking, incomplete because the sum of the forces on the left-hand side is, in fact, equal to the mass times the acceleration of a volume element of the liquid (the so-called "inertia" term). When this term is included, the theoretical E.M. will contain terms that are nonlinear in the field strength. The second approximation pertains to the relaxation effect. When the deformation of the ionic atmosphere is accounted for, all terms of Eq. (24) and the last term of the left-hand side of Eq. (25) contain contributions that are also nonlinear in the field strength. These contributions were omitted in the calculations of Overbeek (24, 25), of Booth (27), and of Wiersema *et al.* (32, 35).

The effect of the inertia term on the E.M. of a sphere was calculated by Booth (85), who found that the correction amounts to 10% for $\zeta = 200$ mV and $\mathbf{X}a = 200$ volts; for a sphere with a radius of 10^{-1}cm, this value of $\mathbf{X}a$ corresponds to a field strength of 2×10^6 volts/cm. A similar result was found recently by Friedman (86) for small ions. The influence of nonlinear terms on the relaxation effect has not been investigated for colloid systems, but from theoretical and experimental work on the Wien effect in electrolyte solutions [cf. Harned and Owen (87)] it is known that these terms are completely negligible at field strengths below 10^3 volts/cm.

Since in ordinary electrophoresis experiments the field strength does not exceed 10 volts/cm, it is clear that neglect of all nonlinear terms is completely justified. Of course, this also follows from the fact that deviations of Ohm's law are not observed in colloidal solutions at moderate field strengths.

J. Effect of Colloid Concentration

Strictly speaking, all theories discussed above can be applied only in the limiting case of infinitely small colloid concentration. When this concentration is not small, various complications can be expected. First, when the combined volume of the migrating colloid particles is appreciable, the effect of backflow of the solvent cannot be neglected. This flow causes a decrease in the observed E.M. From their measurements on soap micelles, Stigter and Mysels (44) concluded that this effect is responsible for a large part of the concentration dependence. Further complications

may arise from interactions between the colloid particles. A discussion of these effects was given by Abramson *et al.* (79). When the concentration of particles is so high that their ionic atmospheres overlap, the electric repulsion affects the E.M. These interactions are most likely to occur at low ionic strength, and especially in polyelectrolyte solutions containing only counterions. Hydrodynamic interaction is present when the disturbance of the solvent created by a moving colloid particle extends as far as the locations of neighboring particles. These interactions have a comparatively long range because the hydrodynamic disturbance is inversely proportional to the distance from the particle (86), whereas the double layer potential, ψ, decreases exponentially with this distance.

Since, at present, our theoretical understanding of these complications is very insufficient, the only practical approach to a quantitative interpretation of observed E.M. values is to extrapolate these values to zero colloid concentration, or at least to make sure that one measures in a region where the E.M. does not depend significantly on this concentration. For the case of soap micelles, the extrapolation procedure is discussed by Stigter and Mysels (44). The case of polyelectrolytes with or without added salt has been discussed by Möller *et al.* (88).

K. CONCLUSIONS

From the discussion given in this section we conclude that the simple model of Section III has a wider range of applicability than one might expect. One of the reasons is that some of the complications are quite negligible (Brownian movement, nonlinear terms) or can be often avoided experimentally without much trouble (mixtures of electrolytes, colloid concentration). In other cases, complications are diminished by the nature of the systems (interfacial properties preventing transfer of electric charge or momentum across the interface, random orientation causing elongated particles to behave rather like spheres).

Nevertheless, the present state of the theory leaves a number of things to be desired. As outstanding examples we mention the absence of relaxation theories for more complicated systems (see also Section V), the difficulties concerning the inner region of the double layer (which make the calculation of charge from ζ-potential rather hazardous) and uncertainty about the viscoelectric effect. Further experiments would probably make clearer what sort of theoretical developments are most needed. In this connection we should like to mention again that not much progress can be made by applying one or two corrections to the theory while neglecting others that can be expected to be of the same order of magnitude. In such cases it may be better to use the simple theory while keeping in mind that the results are semiquantitative.

V. Electrophoresis of Polyelectrolytes

A. Introduction

In many cases the objects of electrophoresis research will be natural or synthetic polyelectrolytes. Quite often the model of rigid, nonconducting spherical particles with a uniformly distributed surface charge will be unrealistic, and the concept of ζ-potential, which applies well to metal, silver halide, or oil particles in electrolyte solutions, loses much of its usefulness. But an analysis in terms of the four forces, k_1, k_2, k_3, and k_4, such as we have used in Section II as the basis of all further calculations, remains also valid for polyelectrolytes, as does the fact that, compared to the three other forces, k_4, the relaxation effect, produces terms of higher order in the charge density or the surface potential.

The aim of the determination of the E.M. will often be the calculation of an "electrokinetic charge," in order to compare it with an "analytical charge." If the two are different, some conclusion may be drawn about the location of the surface of shear, or about specific adsorption of ions. More generally, the aim of electrophoresis research may be to understand the E.M. as a function of the degree of dissociation, α, of the polyelectrolyte. the ionic strength. *I,* and the types of electrolyte used, in terms of the assumed structure of the polyelectrolyte ions. In this section we shall first consider the electrophoresis of proteins, then deal with synthetic linear polyelectrolytes of the polyacrylic acid type, and finally say a few words about nucleic acids. Section V,E of this chapter will indicate an empirical method to determine the relaxation effect, which can be used in cases where the theoretical calculation is not (yet) possible.

B. Proteins

Frictional behavior of protein molecules has often been interpreted in terms of hydrated ellipsoids of revolution. [For a survey of methods and the relevant equations, cf. Scheraga (89).] Although the available data are frequently not accurate and not extensive enough to allow very precise conclusions, it seems fair to state that native protein molecules are only moderately hydrated (usually less than 0.5 gm of water per gram of protein) and that many of these hydrated molecules are not very asymmetric (axial ratio less than 1 : 5). As long as specific indications to the contrary are absent it seems reasonable to interpret electrophoresis data by assuming the molecules to be massive particles, with known friction constant (e.g., from diffusion or sedimentation data) and a shape not too far away from the spherical. As the protein charge is usually low, and electrophoresis is carried out at relatively high ionic strength, the ζ-

potential of such a particle can be expected to be low. Consequently the relaxation effect is not very important, but the electrophoretic retardation ($\mathbf{k}_3$) should not be neglected.

The most obvious interpretation of the E.M. of proteins is, therefore, based on Henry's electrophoresis equation [see Section III,D,2; Eq. (32)] or, if the relaxation effect should not be quite negligible, on Overbeek's equations (33, 34). If it is known that the particles deviate strongly from the spherical shape, the equations (45) to (47) for randomly oriented cylinders as discussed in Section IV,G can be used, provided the relaxation effect is small. If a substantial influence of relaxation is expected, it is better to use the theory for spherical particles with relaxation. This is all the more justified since, without relaxation, the mobilities of cylinders and of spheres of equal volumes are nearly equal (cf. Section IV,G, Table II).

These interpretations lead to values of the ζ-potential which can further be converted into electrophoretic charges, as indicated in the end of Section III,D,5 for spherical particles. For extremely elongated particles the calculations of Abramson *et al.* (78, 79) and of Dube (80) for cylinders may be used although their validity is restricted to low potentials. For thin double layers ($20/\kappa <$ main radius of curvature) the relation between charge and potential for flat plates will be the best approximation (cf. Section IV,G).

Interpretations of protein molecules on this basis lead to electrokinetic charges which are of the same order of magnitude as the titrated charge (binding of H^+ and OH^- ions), show a similar dependence on pH and on ionic strength, but are in general somewhat lower than the titrated charge. A number of examples are cited by Brown and Timasheff (90). [Cf. also Overbeek (91).]

The difference between electrokinetic charge and titrated charge can be explained qualitatively by binding of ions other than H^+ or OH^- and by assuming that a part of the counterions is located within the surface of shear, with the result that the electrokinetic charge is diminished. A more quantitative analysis in this direction, especially with variation of ionic strength, might be rewarding. It could lead to information about the location of the surface of shear and this should be consistent with data on friction constants derived from sedimentation, diffusion, and viscosity.

That ion binding occurs in many cases, shows up clearly in the shift of the isoelectric point with ionic strength (cf. Reference 90). At the isoelectric point the interpretation of electrophoresis is very simple, indeed, because $\mathbf{U} = 0$ implies $\zeta = 0$ and $Q = 0$, independent of the shape of the particle. A shift of the isoelectric point with ionic strength can

only be understood if ions are adsorbed by the protein molecules

It has been suggested by several authors that the E M of a particle with a rough surface can be described with the usual electrophoresis equations simply by using for the value of the radius in the equations the radius of curvature of the bumps and extensions, rather than the overall radius of the particle Examples are the statement by Abramson (92) that for certain proteins "it seems necessary that (κa) remains unchanged each molecule taking its own (κa) along with it" on adsorption on particles of a much larger size It had been found that the E M of these proteins did not change on adsorption but the overall radius had obviously been increased greatly and at the given ionic strength this should have increased the mobility appreciably

In a similar way Brinton and Lauffer (93) suggest that the mobility of flagellated bacteria or of erythrocytes, should be interpreted by using the radii of the flagellae or of the surface roughness of the erythrocytes rather than the virtually infinite radii (compared with $1/\kappa$) of the bacteria or erythrocytes as a whole

In general one should expect, of course that a rough surface has a larger friction and thus needs a higher charge than does a smooth surface in order to produce the same mobility and qualitatively the assumption of a small radius of curvature works in the right direction Quantitatively however, the picture is not consistent It neglects the contribution of the large particle to the over-all friction and also neglects the overlap of the double layers on the flagellae, the individual bumps on a rough surface etc which should lead to an increase of the effective electrophoretic radius with decreasing ionic strength

Moreover, in a recent careful reappraisal of data on electrophoresis of large particles covered by proteins Bull *et al* (94, 95) conclude that in this case the effective radius is virtually infinite, rather than corresponding to the radius of the native protein molecule The relatively low charge corresponding to this large radius is explained by assuming that part of the charge of the adsorbed protein is neutralized on the substrate and not available as electrokinetic charge

C Random Coil Polyelectrolytes

To interpret the electrophoresis of randomly coiled polyelectrolytes such as polyacrylate or gum arabic in terms of a hard impermeable sphere is completely unrealistic Hermans and Fujita (96) and Overbeek and Stigter (97) have treated the electrophoresis of an open coil taking into account that a part of the counterions is inside the coil region and that these ions are mobile in the electric field, but omitting the relaxation effect Longworth and Hermans (98) have given an approximate treat-

ment of the relaxation effect, essentially based on the deformation of the applied electric field, resulting from the difference in conductivity inside and outside the coil.

In all these treatments the polymer is considered as a uniform distribution of segments or monomers in a spherical region of radius R, and the small ions are supposed to be distributed inside and outside this sphere in accordance with the linear approximation of the Poisson-Boltzmann equation. Thus the total charge Ze of the polyelectrolyte molecule is supposed to be neutralized by a charge $-Z_{eff}e$ outside the coil and by a charge $-(Z - Z_{eff})e$ inside the coil. For a calculation of $Z_{eff}e$, cf. References 99–101. The liquid inside the coil is assumed to have the same viscosity as the bulk liquid. It is entrained by the electric force acting on the countercharge inside the coil and in its turn entrains the coil by hydrodynamic forces on the individual segments of the coil that are considered as particles with a friction constant f. This treatment is similar to the calculation of the friction constant F of the whole coil in diffusion or sedimentation as given by Debye and Bueche (102) and by Brinkman (103).

The final electrophoresis equation as obtained by Overbeek and Stigter is

$$\frac{U}{X} = \frac{Z - Z_{eff}}{Nf} e + \frac{Z_{eff}}{F} e - \frac{Z_{eff}}{6\pi\eta R} \frac{\kappa R}{1 + \kappa R} e \tag{50}$$

in which N is the number of segments per coil, and F is given by Debye and Bueche's expression

$$F = \frac{9}{2\sigma^2} \frac{1 - \tanh \sigma / \sigma}{1 + (3/2\sigma^2)(1 - \tanh \sigma/\sigma)} Nf \tag{51}$$

with

$$\sigma^2 = 3Nf / 4\pi\eta R$$

Expression (50) is slightly less correct than the expression obtained by Hermans and Fujita, but in practice the differences are quite small and expression (50) has the advantage that the different terms can be interpreted separately. The first term on the right-hand side of Eq. (50) represents the combined effect of the countercharge inside the coil plus an equivalent part of the charge on the coil segments. The second term would give the motion of the coil if it had just an effective charge of $Z_{eff}e$ and nothing else, and the third term represents the electrophoretic retardation caused by the countercharge outside the coil. Figure 7 gives a good idea of the mobility as influenced by κR and by the ratio $6\pi\eta R / Nf$. This last ratio is a measure of the degree of free drainage of the coil. If it is small, drainage is negligible and the coil behaves as a

$$\frac{U}{X} \cdot \frac{Nf}{Ze}$$

$$\frac{6\pi\eta R}{Nf} \quad \infty, 3 \ 1 \ .05 \ .028$$
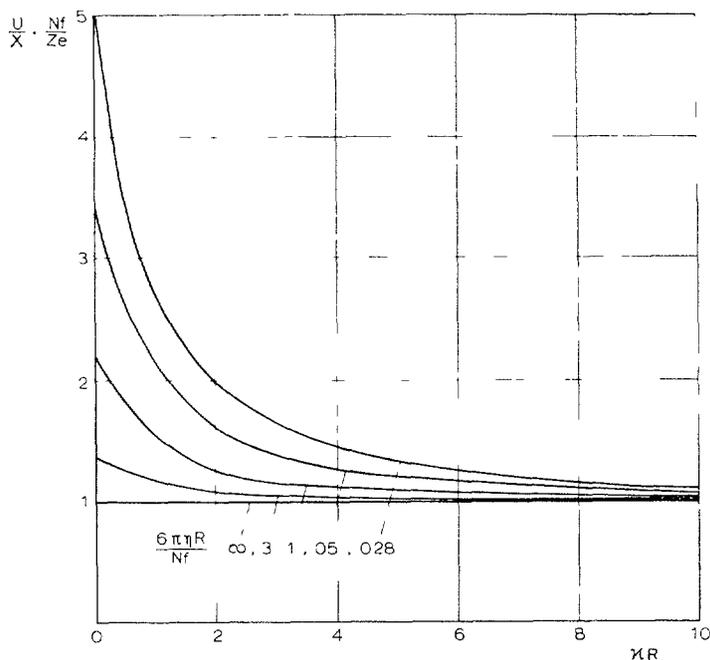
Fig. 7. Electrophoretic mobility of spherical coil for various degrees of drainage.

hard impermeable sphere with a charge equal to $Z_{eff}e$. In that case the first term on the right-hand side of Eq. (50) can be neglected, F becomes equal to $6\pi\eta R$, and the last two terms of Eq. (50) are equivalent to the combination of Eqs. (19) and (36), i.e.. reduce to the Hückel case (no relaxation, no deformation of the applied field). If $6\pi\eta R/Nf$ becomes very large, the drainage is virtually complete, the electrophoretic retardation becomes negligible and the electrophoretic mobility approaches

$$U/X = Ze'Nf \tag{52}$$

The above model ceases to be realistic when the double layers are compressed to such an extent that they screen the individual charged sites of the particle effectively from one another. In those circumstances the E.M. would decrease below the limit Ze/Nf shown in Fig. 7 and, with increasing electrolyte content, finally go to zero as a limit. This would occur when $1/\kappa$ is of the same order as a, the "radius" of the charge-carrying group. In a schematic way Fig. 8 shows two different curves of electrophoresis against κ, one for relatively large radius (a_1) and one for relatively small radius (a_2).

No quantitative calculations have been made for this case, but the elec-

trophoresis of a cylinder might be a useful approximation. Figure 9 shows how a polymer coil surrounded by a highly condensed double layer can be considered as a combination of randomly oriented cylinders. One of the obvious consequences of this model is that the E.M. becomes independent of molar mass.
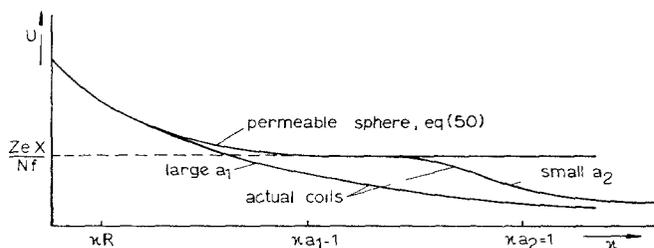
FIG. 8. Schematic electrophoresis curves for a permeable sphere and for polyelectrolyte coils with individual charged segments; a_1 and a_- are the radii of the segments
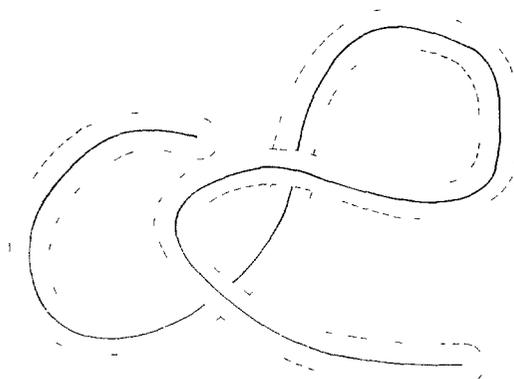
FIG. 9. Schematic picture of coiled polyelectrolyte with compact double layer.

The omission of the relaxation effect forms a serious drawback to most calculations of the electrophoresis of coiled polyelectrolytes. This might not be too bad for low electrolyte content and low charge density, but for high electrolyte content the effect may be important. In Section V,E, we shall discuss a direct experimental determination of the relaxation effect which may help to solve this difficulty.

A striking feature in most experiments on electrophoresis and conductance of polyelectrolytes is the fact that the influence of molar mass is so small. This was found already in Kern's early experiments (104),

and was later confirmed by many others. Schindewolf (105, 106) showed with polyphosphates that, for very small molar mass, the influence of molar mass is strong, but that it levels off soon.

The independence of molar mass is in agreement with the model of a freely drained coil, but also with any model in which the E.M. is governed by the local situation around the charged site. On this same basis, one would expect the E.M. to be proportional to the charge of the polymer (at constant molar mass). In practice, however, the dependence on the charge is much less pronounced. Explanations that have been offered for this effect are:

1. At lower charge density the coil contracts and its friction diminishes. This explanation, however, is difficult to reconcile with the virtual independence of molar mass.

2. Counterions are bound to the coil at the higher charge densities.

3. The size of an elementary segment depends on the charge on the chain. It corresponds to that section of the chain that carries one charged group and its friction can be described as that of a prolate ellipsoid with a diameter independent of its length. This hypothesis was formulated by Noda *et al.* (107) and applied with considerable success to data on the E.M. of sodium polyacrylates in 0.1 M NaCl. They calculate 6 Å as the diameter of the ellipsoid (sphere in case of the monomer of a fully charged polymer) from electrophoresis data—a very reasonable value compared to the actual size of the monomer.

D. Nucleic Acids

Since nucleic acids are highly charged and rather stiff in the native state, their electrophoresis can probably best be described by the randomly oriented cylinder model (108, 109). After denaturation they may coil up and then might be more suitably described as random coils. So far very little work has been done on quantitative interpretations of nucleic acid mobility.

E. Empirical Determination of the Relaxation Effect

Just as with ordinary electrolytes, some information on the relaxation effect can be obtained from measurements at high frequency (Debye-Falkenhagen effect) or high field strength (Wien effect). The low-frequency dielectric constant is also, in part, determined by the asymmetry of the double layer. Unfortunately none of these methods is easy to exploit. The Wien effect gives a mixture of relaxation with part of the electrophoretic retardation. The low-frequency dielectric constant contains dipole contributions next to the relaxation effect, and only if the time of

relaxation of the dipole orientation is sufficiently different from that of the double layer, dielectric constant or dielectric loss measurements would give a direct access to the relaxation effect. Moreover, in all these cases the low molecular weight electrolytes also make a contribution, and separation of this effect from that due to the polyelectrolyte is not simple. Nevertheless it is felt that more work both theoretical and experimental in this direction would be useful. We want to mention papers by Schwarz (110) and by Schurr (111) on the dielectric dispersion of spherical particles in electrolyte solution, where earlier literature is cited.

Möller *et al.* (88) have shown that in favorable cases the influence of relaxation can be calculated from transference data. The general idea on which this method is based is as follows. The electrophoretic retardation results from the hydrodynamic pattern around the particle. It is caused by the action of the applied field on the surface charge and on the space charges, but it is *independent of the nature and the mobility of the counterions.* The relaxation effect, on the contrary, results from a lowering of the field acting on the particle and on the counterions and it will *decrease the velocity of an ion with a high mobility much more than that of an ion with a low mobility.* Consequently, the two effects can be separated by measuring conductivity and transference, using the same polyion with counterions of different mobilities.

If counterions are used that are not specifically adsorbed and if the total electrolyte content is low, the space-charge distribution and, therefore, the electrophoretic retardation should be independent of the counterions used. The deformation of the field, and thus the relaxation effect, described as a lowering of the field strength by an amount X_{relax}, which has the opposite direction of the applied field X, are also nearly independent of the ionic mobility (see Section III,D,3).

It is also confirmed experimentally that the mobilities of the polyion are independent of the choice of the counterion. See Strauss and Ross (112) for polyphosphates and Möller *et al.* (88) for bovine serum albumin.

Therefore, if we consider a negatively charged colloid particle and counterions which are in one case Li^+ and in the other, K^+ (thus with rather widely differing mobilities), we expect the velocity of the particle to be

$$U_{particle} = (U^0_{particle} - U_{electroph}) \left(1 - \frac{X_{relax}}{X} \right) \tag{53}$$

where $U^0_{particle}$ is the velocity in the field X in the absence of any retarding effects, $U_{electroph}$ is the electrophoretic retardation, and X_{relax} the relaxation field, both independent of the type of counterion.

For the velocity of the counterions we may expect

$$U_K = (U_K^0 - U_{K\ \text{electroph}})\left(1 - \frac{X_{\text{relax}}}{X}\right) \tag{54}$$

$$U_{Li} = (U_{Li}^0 - U_{Li\ \text{electroph}})\left(1 - \frac{X_{\text{relax}}}{X}\right) \tag{55}$$

where the symbols have meanings analogous to those used in Eq. (53). The X_{relax} is the same for the colloid particle and the counterion, because the relaxation effect is based on a force of interaction between the particle and an electrically equivalent amount of counterions, so that it must obey Newton's principle that action equals reaction. On the other hand, the electrophoretic retardations for the two types of counterions are the same, because the two ions are in the same field of flow. But the electrophoretic retardation for the ions may be, and in general is, different from that for the particle.

Subtraction of Eqs. (54) and (55) leads to

$$1 - \frac{X_{\text{relax}}}{X} = \frac{U_K - U_{Li}}{U_K^0 - U_{Li}^0} \tag{56}$$

and, consequently, a measurement of the mobility of the *counterions* may lead to an empirical estimate of the relaxation effect.

Since the mobility of the polyion is independent of the choice of the counterion, the difference between the mobilities of the cations is proportional to the difference of the equivalent conductances of the poly-salts. Consequently, Eq. (56) may be written

$$1 - \frac{X_{\text{relax}}}{X} = \frac{\Lambda_{K-\text{poly}} - \Lambda_{Li-\text{poly}}}{\lambda_K^0 - \lambda_{Li}^0} \tag{57}$$

The fact that the right-hand side of Eq. (57) is independent of the choice of the cations was demonstrated by Eisenberg (113) for polymethacrylic acid. In this equation $\Lambda_{K-\text{poly}}$ is the equivalent conductance of the potassium salt of the polyion, and λ_K^0 the limiting ion conductance of the K+ ion at infinite dilution.

The above considerations are most straightforward for solutions of a pure polysalt without added low molecular weight electrolyte. In the presence of salt the situation is more complicated, since both counterions and co-ions are involved in the relaxation effect, but, since the counterions are drawn toward the polyion and the co-ions are pushed away, the main effect is due to the counterions in the neighborhood of the polyion.

Assuming that the total conductance of such a solution can be split

up in the conductance of the supporting solution (containing all co-ions and an equivalent amount of counterions, with mobilities they would have in a colloid free solution of the same concentration) and the polysalt, then the above equations should be applied to the contribution of the polysalt to the conductance and lead to acceptable values of the relaxation correction. In the measurements by Möller *et al.* (88) the calculated relaxation correction, X_{relax}/X, for bovine serum albumin varied between 2 and 15%, depending on the charge on the particles, their concentration, and the concentration of the supporting electrolyte. The agreement with calculated values (see Table III) of the relaxation effect for

TABLE III

RELAXATION EFFECT FOR BOVINE SERUM ALBUMIN[a]

Elementary charges per protein molecule	κa	ζ-potential (mV)	$1 - \dfrac{X_{relax}}{X}$ [Eq. (57)]	Relaxation retardation of rigid sphere[b]
10.83	0.50	30	0.93	0.95
10.83	0.22	41.4	0.95	0.97
10.83	0.10	47.5	0.97	0.98
22.1	1.0	47	0.88	0.95
22.1	0.5	69	0.88	0.90
22.1	0.25	87	0.90	0.92
22.1	0.178	94	0.93	0.91

[a] Comparison between relaxation effect calculated from experiments on Li and K salts of bovine serum albumin and relaxation effect calculated for a rigid sphere (radius, $a_r = 34.5$ A) of the same charge. The charge was obtained by adding LiOH or KOH to iso-ionic bovine serum albumin. The ζ-potential was calculated from the charge assuming complete absence of ion binding.

[b] Calculated as discussed in Section III of text.

rigid spheres as described in Section III is not perfect, but good enough to make this an attractive method to obtain an estimate of the influence of relaxation on conductance and electrophoresis. Especially in the case of coiled polyelectrolytes, where a complete theory is missing, this is a valuable asset.

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