Calculation of the Electrophoretic Mobility of a Spherical Colloid Particle

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ABSTRACT

A new calculation of the relation between the electrophoretic mobility and the ζ-potential of a spherical colloid particle is presented. The model consists of a rigid, electrically insulating sphere surrounded by a Gouy-Chapman double layer. The appropriate differential equations (which account for both electrophoretic retardation and relaxation effect) have been solved without approximations on an IBM 704 computer.

The theoretical assumptions and the basic equations are stated. A detailed account of the solutions of the equations is published elsewhere. The present paper contains the complete results. Comparison of these results with those of Overbeek and of Booth shows that, for high ζ-potential and $0.2 < \varkappa a < 50$, their approximations generally overestimate the relaxation effect. The application to practical cases (especially colloid particles in solutions of 1-1 electrolytes) is discussed extensively. Finally, the theoretical results are compared with experimental data published by others.

INTRODUCTION

The calculation of the ζ-potential from measurements of the electrophoretic mobility (E.M.) requires a theoretical relation between the two quantities. The oldest relation of this kind, which was derived by von Helmholtz (1) and improved by von Smoluchowski (2), reads

$$\frac{U}{X} = \frac{\epsilon \zeta}{4 \pi \eta}. \qquad [1]$$

In this equation, U is the electrophoretic velocity, X is the strength of the applied d.-c. field (U/X is the electrophoretic mobility); ϵ and η represent the dielectric constant and the viscosity coefficient, respectively, of the solution surrounding the colloid particles.

More recent work by Hückel (3), Henry (4), Overbeek (5), and Booth (6) has shown that the validity of Eq. [1] is rather restricted. In the case of a spherical colloid

particle, it is valid only when $\varkappa a \gg 1$, where a is the radius of the particle and $\varkappa$ is the reciprocal thickness of the surrounding ionic atmosphere. For moderate values of $\varkappa a$ (say, $0.2 < \varkappa a < 50$), the so-called relaxation effect leads to important corrections, which increase with increasing ζ-potential. This was found by Overbeek (5) and, independently, by Booth (6). Both authors expressed the E.M. as a power series in the ζ-potential; however, because of mathematical complications they were able to calculate only a few terms of the series. Quantitative validity of their results could therefore be claimed only for small ζ-potentials ($\zeta < 25$ mv.).

The results of a more general calculation, which was carried out by means of an IBM 704 digital computer, will be presented in this paper. The physical assumptions, which are the same as those used in the work of Overbeek (5), are as follows:
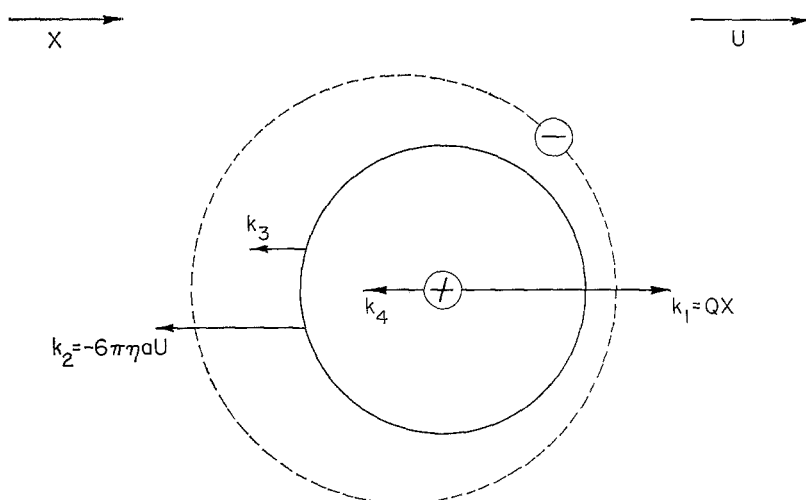
a. The interaction between colloid par-

FIG. 1. Forces in electrophoresis. The dotted line represents the ionic atmosphere.

ticles is neglected and only a single particle is considered.

b. This particle (plus the adjacent layer of liquid that remains stationary with respect to it) is treated as a rigid sphere.

c. The dielectric constant is supposed to be the same everywhere in the sphere.

d. The electric conductivity of the sphere is assumed to be zero. This implies that the charge within the surface of shear does not move with respect to the particle when the d.c. field is applied.

e. The charge of the sphere is supposed to be uniformly distributed on the surface.

f. The mobile part of the electric double layer is described by the classical Gouy-Chapman theory.

g. The dielectric constant of the liquid surrounding the sphere is assumed to be independent of position.

h. Only one type of positive and one type of negative ions are considered to be present in the ionic atmosphere.

i. The viscosity coefficient of the liquid surrounding the sphere is supposed to be independent of position.

j. Because colloidal solutions follow Ohm's law at the moderate field strengths (a few volts per centimeter) that are employed in electrophoresis experiments, only terms that are linear in the field are taken into account in the computation.

k. The Brownian motion of the colloid

particle is neglected. (The order of magnitude of this effect has been estimated by means of a calculation that was published elsewhere (7a)).

This paper is written for readers who are primarily interested in results and applications. Therefore, the mathematical problem will just be stated here. The analytical and numerical methods that were used in solving the problem can be found elsewhere (7a–9).

STATEMENT OF THE PROBLEM

In the remainder of this paper, the colloid particle plus the adjacent layer of liquid is called "the sphere." The electric charge of the sphere is assumed positive; consistent sign reversal makes the results applicable to a negatively charged particle.

Let us first consider the forces acting on the sphere when it is in uniform electrophoretic motion (Fig. 1). The force exerted by the d.c. field, X, on the charge, Q, of the sphere is

$$k_1 = QX. \qquad [2]$$

The second force is the Stokes friction,

$$k_2 = -6\pi\eta aU, \qquad [3]$$

where η is the viscosity coefficient of the liquid surrounding the sphere, U is the electrophoretic velocity, and a is the radius of the sphere (i.e., the distance from the center

of the colloid particle to the surface of shear).

The two remaining forces are caused by the "ionic atmosphere." The d.c. field exerts on the ions in this atmosphere a force which is transferred to the solvent molecules. The resulting flow of solvent causes a retarding force, k_3, on the sphere (electrophoretic retardation). Furthermore, in the stationary state which is present shortly after the application of the d.c. field, the center of the ionic atmosphere lags behind the center of the particle. This causes an electrical force, k_4, on the particle, which is, in most cases, also a retarding one (relaxation effect).

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 (10). In the latter theory, no important error results when the two effects are superimposed linearly; for colloidal particles the mutual interactions between the effects are considerable. In this case, k_3 must be calculated for an asymmetric atmosphere and in the evaluation of k_4 the velocity distribution in the liquid must be taken into account explicitly.

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

$$k_1 + k_2 + k_3 + k_4 = 0. \qquad [4]$$

Equations [2]–[4] can be combined to give

$$U = \frac{1}{6\pi\eta a} (QX + k_3 + k_4). \qquad [5]$$

The forces k_3 and k_4 are functions of the ζ-potential and of several other parameters, such as the radius of the sphere and the charges, concentrations, and mobilities of the ions in the double layer. Because these other parameters are known in most cases, the relation between U and ζ can be found by calculation of the forces k_3 and k_4.

As a starting point, we shall write down expressions for the total electrical force, $k_1 + k_4$, and for the total hydrodynamic force, $k_2 + k_3$. The first expression reads:

$$k_1 + k_4 = \iint \sigma(-\nabla\Lambda)_{ax} \, dA, \qquad [6]$$

where dA is an element of the surface of shear; σ is the surface charge density defined by $4\pi a^2 \sigma = Q$ (where Q includes both the particle charge and other charges that may be bound within the surface of shear); and Λ is the total electric potential caused by the charges on the sphere and in the liquid and by the external field. Hence, $-\nabla\Lambda$ is the total electric force on a unit charge. In Eq. [6], the subscript a denotes that we take the force at the surface of shear, and x specifies the component of this force in the direction of the d.c. field.

The total hydrodynamic force can be expressed as

$$k_2 + k_3 = \iint p_{ax} \, dA, \qquad [7]$$

where p_{ax} is the stress on an element of the surface of shear in the direction of the d.c. field. This stress is a rather complicated function of u, the velocity of the liquid with respect to the center of the sphere, and of p, the hydrostatic pressure in the liquid.

It appears that more explicit expressions for the forces (and hence, for U) can be found when Λ, u, and p are known as functions of position. The functions are governed by a set of differential equations that will be given here without derivations. More details concerning these equations can be found in the publications of Henry (4), Overbeek (5), and Booth (6), and in references 7a and 8.

In the formulation of the differential equations and boundary conditions, the center of the sphere is considered as the origin of the coordinate system.

The total electric potential, Λ, which includes the external d.c. field, is governed by Poisson's equation:

$$\nabla^2\Lambda = -\frac{4\pi\rho}{\epsilon} = -\frac{4\pi e}{\epsilon} (z_+ \nu_+ - z_- \nu_-) \quad [8]$$

where ρ is the space-charge density in the liquid, ϵ is the dielectric constant of the liquid, e is the elementary charge, $z_\pm$ are the valences of the ions, and $\nu_\pm$ are their local concentrations (number/cm.³). It is essential that ν_+ and ν_- are not bulk concentrations and not equilibrium concentrations,

but ion concentrations in the distorted atmosphere; by the introduction of these quantities, the relaxation effect enters into the differential equations.

For a complete description of the electric potential, we also need an equation for Λ_i, the potential within the sphere. This is the Laplace equation,

$$\nabla^2 \Lambda_i = 0, \qquad [9]$$

which expresses that there is no space-charge within the sphere.

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

$$\nabla \cdot \left[\mp \frac{\nu_\pm z_\pm e}{f_\pm} \nabla \Lambda - \frac{kT}{f_\pm} \nabla \nu_\pm + \nu_\pm \boldsymbol{u} \right] = 0 \ [10]$$

where $f_\pm$ are the friction coefficients of the ions, k is Boltzmann's constant, and T is the absolute temperature. The first term between the brackets represents the migration of the ions in the electric field. The second term is a diffusion term in which the diffusion coefficients of the ions are written as $kT/f_\pm$, according to a theorem of Einstein (11). The last term expresses that the flow of the liquid gives an extra velocity to the ions. The sum of the three gives the total flow of the ions (concentration times velocity). In the stationary state, the ionic distribution around the sphere remains constant in time; hence, the divergence of the flow is zero.

We observe that the so-called surface conductance, insofar as it occurs outside the surface of shear, is implicitly taken into account by the transport equations. This is so because the insertion of local, not bulk, concentrations into the first term implies that the ionic conductivity in the double layer differs from the bulk conductivity.

Next we come to the hydrodynamic equations, which govern the functions $\boldsymbol{u}$ and p. First, we have

$$\eta \nabla \times \nabla \times \boldsymbol{u} + \nabla p + \rho \nabla \Lambda = 0, \quad [11]$$

where η is the viscosity coefficient of the liquid; Eq. [11] is a Navier-Stokes equation in which the acceleration terms were put equal to zero (cf. references 5 and 7a);

the left-hand side is the sum of the forces acting on a volume element of the liquid. The first term represents the friction between this volume element and surrounding portions of the liquid; the second term expresses that the volume element tends to move towards regions of low hydrostatic pressure; the third term is the electrical force on the ions in the volume element; this force is transferred to the liquid. The third term corresponds to the electrophoretic retardation (k_3); if only the first two terms were considered, the solution of Eq. [11], combined with the integral of the right-hand side of Eq. [7], would give just the Stokes friction (k_2). Finally, we have Eq. [12], expressing that the fluid is incompressible:

$$\nabla \cdot \boldsymbol{u} = 0. \qquad [12]$$

We now have eight differential equations (Eqs. [8] and [9], the two equations [10], the three components of Eq. [11], and Eq. [12]) for the eight unknown functions Λ, Λ_i, ν_+, ν_-, the three components of $\boldsymbol{u}$, and p. Hence, the problem is determinate except for the boundary conditions. Because all equations, except for Eq. [12], are of second order, we need fifteen conditions.

Far from the particle, the electric field equals the external d.c. field. Hence,

$$\lim_{r \to \infty} \Lambda = -Xx, \qquad [13]$$

where r is the distance from the center of the particle and x is the value of the Cartesian coordinate in the direction of the external field. At the surface of shear, $r = a$, the potential obeys the following relations:

$$\Lambda = \Lambda_i \quad \text{at} \quad r = a; \qquad [14]$$

$$\epsilon \frac{\partial \Lambda}{\partial r} = \epsilon_i \frac{\partial \Lambda_i}{\partial r} - 4\pi\sigma \quad \text{at} \quad r = a; \ [15]$$

where ϵ_i is the dielectric constant of the sphere. Furthermore, everywhere within the sphere

$$\Lambda_i \text{ is finite or zero.} \qquad [16]$$

In the solution far from the particle, the

ion concentrations are equal to $n_\pm$, the bulk concentrations:

$$\lim_{r \to \infty} \nu_\pm = n_\pm . \qquad [17]$$

Because the sphere is nonconducting, and, in the stationary state there is no accumulation of ions at the surface of shear, the r-components of the flow vectors of the ions vanish at $r = a$:

$$r \cdot \left[\mp \frac{\nu_\pm z_\pm e}{f_\pm} \nabla \Lambda - \frac{kT}{f_\pm} \nabla \nu_\pm + \nu_\pm \boldsymbol{u} \right] \qquad [18]$$
$$= 0 \quad \text{at} \quad r = a.$$

Far from the particle, the velocity of the liquid with respect to the particle equals minus the electrophoretic velocity:

$$\lim_{r \to \infty} \boldsymbol{u} = -\boldsymbol{U}. \qquad [19]$$

At the surface of shear, the fluid velocity is zero:

$$\boldsymbol{u} = 0 \quad \text{at} \quad r = a. \qquad [20]$$

Finally, because the effect of gravity is neglected,

$$\lim_{r \to \infty} p = \text{constant}. \qquad [21]$$

Taking into account that Eqs. [17] and [18] each represent two equations, and that Eqs. [19] and [20] each have three components, we have indeed fifteen boundary conditions.

RESULTS AND DISCUSSION

A. DIMENSIONLESS VARIABLES

The results will be reported in terms of dimensionless variables in order to make the tables and graphs applicable to various experimental situations (e.g., different temperatures or solvents).

First, we define the function E by

$$E \equiv \frac{6\pi\eta e}{\epsilon kT} \frac{U}{X}, \qquad [22]$$

where U/X is the electrophoretic mobility (E.M.).

The parameters involved in the computation are z_+, z_-, q_0, y_0, m_+, and m_-; z_+ and z_- are the valences of the small

ions in the solution. The parameter q_0 is defined by

$$q_0 \equiv \varkappa a/\lambda, \qquad [23]$$

where

$$\varkappa^2 \equiv \frac{4\pi e^2 (n_+ z_+{}^2 + n_- z_-{}^2)}{\epsilon kT}$$
$$= \frac{4\pi e^2 N_a c (z_+ + z_-)}{1000 \epsilon kT} \qquad [24]$$

and

$$\lambda^2 \equiv (z_+ + z_-)/2z_- . \qquad [25]$$

Here N_a is Avogadro's number, c is the average electrolyte concentration in equivalents per 1000 cm.[3]. The factor λ, which is unusual, has been included for the following reason. From Eqs. [23]–[25] we find

$$q_0 = \left(\frac{8\pi e^2 c z_- N_a}{1000 \epsilon kT} \right)^{1/2} a. \qquad [26]$$

This shows that at constant equivalent concentration, q_0 is independent of z_+, the valence of the co-ions. The effect of z_+ on the properties of the double layer (including the E.M.) is small. Using the parameter q_0, we may compare numerical results for cases with the same c and z_-, but different z_+, without having to account for trivial changes of q_0.

Furthermore,

$$y_0 \equiv e\zeta/kT, \qquad [27]$$

and

$$m_\pm \equiv \frac{\epsilon kT}{6\pi\eta e^2} f_\pm . \qquad [28]$$

The friction coefficients, f_+ and f_-, of the small ions can be expressed as

$$f_\pm = N_a e^2 \frac{z_\pm}{\lambda_\pm{}^0}, \qquad [29]$$

where $\lambda_\pm{}^0$ are the limiting equivalent conductances of the ions. Hence,

$$m_\pm = \frac{N_a \epsilon kT}{6\pi\eta} \frac{z_\pm}{\lambda_\pm{}^0}. \qquad [30]$$

At this point we wish to mention that, in our calculation, the electrophoretic mobility turns out to be independent of ϵ_i, the dielec-

tric constant of the particle (cf. references 7a and 8).

B. ANALYTICAL APPROXIMATIONS

In the discussion of the numerical results, these results will be compared with analytical approximations derived by previous authors. In order to facilitate this, we shall now write these approximations in terms of dimensionless variables.

By combining Eq. [1] (the approximation of von Smoluchowski) with Eqs. [22] and [27], we obtain

$$E = \tfrac{3}{2}y_0 . \qquad [31]$$

In the same notation, the result of Hückel (3) reads

$$E = y_0 . \qquad [32]$$

The approximation of Henry (4) for a non-conducting particle can be expressed as

$$E = y_0 f_1(\varkappa a). \qquad [33]$$

A graph of the function $f(\varkappa a) \equiv (\tfrac{2}{3})f_1(\varkappa a)$, as well as analytical expressions for this function, can be found in Henry's paper (4).

In the present notation, Overbeek's result (5) for symmetrical electrolytes is written as

$$E = y_0 f_1(\varkappa a) - y_0^3[z^2 f_3(\varkappa a) \\ + \tfrac{1}{2}(m_+ + m_-)f_4(\varkappa a)], \qquad [34]$$

where z is the valence of both ions. For unsymmetrical electrolytes, Overbeek found:

$$E = y_0 f_1(\varkappa a) - y_0^2(z_- - z_+)f_2(\varkappa a) \\ - y_0^3 \frac{z_+ m_+ + z_- m_-}{z_+ + z_-} f_4(\varkappa a). \qquad [35]$$

Tables and graphs of the functions $f_n(\varkappa a)$ were given by Overbeek (5).

The calculation of Booth (6b) is limited to symmetrical electrolytes. His result can be written as:

$$E = y_0 X_1^*(\varkappa a) + y_0^3 \\ \cdot [z^2\{X_3^*(\varkappa a) + Y_3^*(\varkappa a)\} \\ + 3(m_+ + m_-)Z_3^*(\varkappa a)] \qquad [36] \\ + y_0^4\{3z(m_+ + m_-)Z_4^*(\varkappa a)\}.$$

The function $X_1^*(\varkappa a)$ is identical with $f_1(\varkappa a)$ in Eqs. [33]–[35]. Graphs of the functions $X_3^*(\varkappa a)$, $Y_3^*(\varkappa a)$, $Z_3^*(\varkappa a)$, and $Z_4^*(\varkappa a)$ are given in Fig. 2 of Booth's paper (6b).

In a recent paper (12), Pickard arrives at a result which is essentially that of Hückel (Eq. [32]). A more detailed discussion of Pickard's calculation is given in reference 8.

C. NUMERICAL RESULTS FOR 1-1 ELECTROLYTES

The differential equations given in Part A were solved by means of an IBM 704 computer for a number of combinations of the parameters z_+, z_-, q_0, y_0, m_+, and m_-. In this Part we shall give the computer results for $z_+ = z_- = 1$. We shall first consider how the electrophoretic mobility depends on q_0 and y_0; the effect of m_+ and m_- (which is relatively small) will be discussed later.

In Table I, E is given as a function of q_0 and y_0. In all computations reported in this table, m_+ and m_- were chosen equal to 0.184. In aqueous solutions at 25°C., this corresponds to limiting mobilities of 70 ohm^{-1} cm.^{2} eq.$^{-1}$. In Table I, the actual computer results (given in 4 digits) are combined with interpolated values (given in 3 digits). No data were obtained for $y_0 > 6$, because in this region the computer program failed to give convergent results. The values for $q_0 < 0.1$ and for $q_0 > 50$ were found by extrapolation, taking into account that Overbeek's equation [34] is valid in the limiting cases $q_0 \to 0$ and $q_0 \to \infty$. In the region $q_0 < 0.1$, this extrapolatoin can be done easily, for, at $q_0 = 0.1$, the computer results already coincide with those of Overbeek (cf. Fig. 4). In the region $q_0 > 50$, the extrapolations are less accurate, but it is unlikely that the errors exceed a few per cent. The data of Table I are graphically represented in Fig. 2.

In Figs. 3 and 4, some values of E, taken from Table I, are compared with the analytical approximations [33], [34], and [36]. For all cases involved here, $m_+ = m_-$, with the result that the last term of Booth's equation [36] vanishes. Therefore, the discrepancies between the curves labeled III and IV, representing Eqs. [34] and [36], are caused only by

TABLE I

E AS A FUNCTION OF q_0 AND y_0 FOR 1-1 ELECTROLYTES. $m_+ = m_- = 0.184$

Computer results are given in 4 digits, interpolated values in 3 digits

| y_0	$q_0 = 0$	0.01	0.02	0.05	0.1	0.2	0.5	1	2	5	10	20	50	100	200	500	1000	∞	y_0
1	1.00	1.00	1.00	1.00	0.997	0.996	0.99	1.009	1.04	1.134	1.22	1.325	1.418	1.45	1.47	1.49	1.50	1.50	1
2	2.00	2.00	2.00	1.99	1.971	1.955	1.92	1.912	1.93	2.086	2.27	2.510	2.756	2.87	2.93	2.97	2.99	3.00	2
3	3.00	2.99	2.98	2.96	2.904	2.845	2.71	2.625	2.60	2.742	3.06	3.428	3.921	4.20	4.34	4.45	4.48	4.50	3
4	4.00	3.98	3.95	3.90	3.775	3.638	3.36	3.129	2.99	3.076	3.43	3.963	4.790	5.38	5.68	5.90	5.97	6.00	4
4.50										3.144									4.50
4.75										3.161									4.75
5	5.00	4.97	4.92	4.80	4.585	4.310	3.80	3.436	3.199	3.169	3.470	4.098	5.250	6.22	6.88	7.33	7.46	7.50	5
5.50													5.309						5.50
6	6.00	5.94	5.86	5.66	5.382	4.846	4.11	3.628	3.27	3.08	3.347	3.937	5.266	6.64	7.90	8.73	8.94	9.00	6
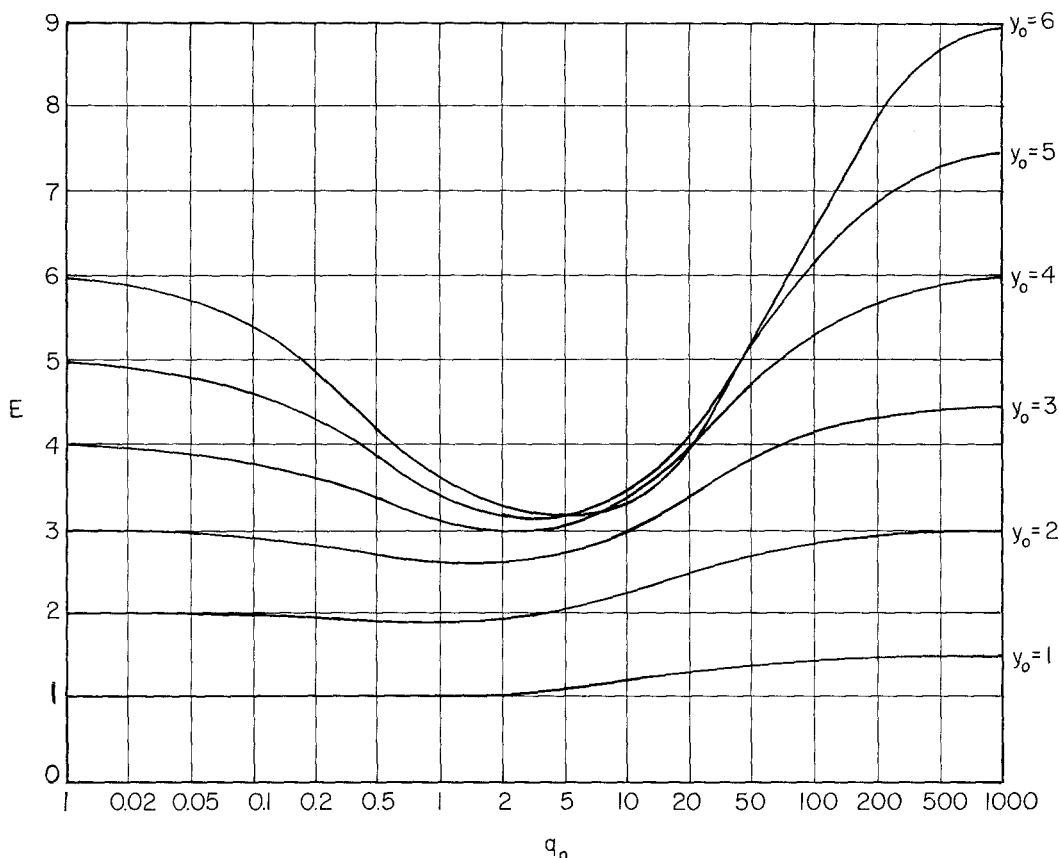
FIG. 2. E as a function of q_0 for different values of y_0. $z_+ = z_- = 1$, $m_+ = m_- = 0.184$. For corresponding numerical data see Table I.

the differences between the coefficients of $y_0{}^3$ in both equations.

The curves labeled II in Figs. 3 and 4 have been included for the following reason. The numerical computations were carried out by means of successive approximations; the first approximation, in which the relaxation effect is neglected, is actually a numerical calculation of the electrophoretic retardation (this point is discussed more extensively in references 7a and 8). It is therefore of interest to compare this first approximation with the result of Henry (Eq. [33]), who also neglected the relaxation effect. The differences between the curves I and II are caused by the fact that Henry (4) had used a linearized Poisson-Boltzmann equation, whereas we included the nonlinear terms of this equation. Figures 3 and 4 show that the contribution of these nonlinear terms to the

electrophoretic retardation is remarkably small. This is confirmed by the calculation of Booth (6b); the function $X_3{}^*(\varkappa a)$ in Eq. [36], which (to his approximation) represents the nonlinear terms of the electrophoretic retardation, is small compared to the other terms in the coefficient of $y_0{}^3$.

The conclusions of Overbeek (5) and of Booth (6) concerning the relaxation effect are at least qualitatively confirmed by the numerical computations. The relaxation correction is appreciable and increases sharply with increasing ζ-potential. The correction is largest for moderate values of q_0 and is negligible when q_0 is very small or very large.

Figure 3 shows that, for moderately low values (up to $y_0 = 2.5$) of the ζ-potential, our numerical results are in quantitative agreement with the approximations of
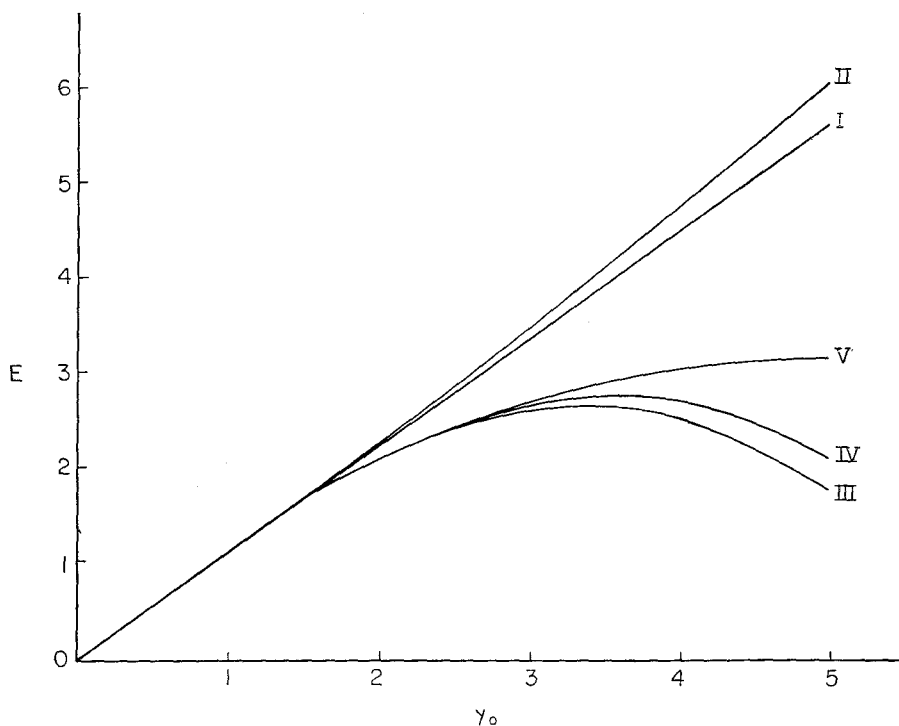
FIG. 3. E as a function of y_0 for $z_+ = z_- = 1$, $q_0 = 5$, $m_+ = m_- = 0.184$. I: Eq. [33] (Henry); II: first approximation of numerical computations; III: Eq. [34] (Overbeek); IV: Eq. [36] (Booth); V: numerical computations.

Overbeek and of Booth. The same is true for other values of q_0. This provides a check on the numerical computations.

For higher values of the ζ-potential, it appears that the relaxation effect is overestimated by the analytical approximations [34] and [36]. For $q_0 = 5$, the difference between the approximations and the numerical results becomes appreciable for $y_0 > 3$. However, this difference has a maximum at $q_0 = 5$ (cf. Fig. 4); therefore, the approximations are more useful in cases when q_0 is smaller or larger than 5.

It is also of interest to know whether the curve of E vs. y_0 passes through a maximum, for, if this is the case, two different values of the ζ-potential correspond to a given value of the E.M. Such a maximum is implied by the equations of Overbeek and of Booth. According to the numerical results (Table I), E increases steadily with y_0, except for $q_0 = 20$ and $q_0 = 50$, where a maximum is observed. Therefore, when E is given, the value of y_0 is unambiguously determined by

the data of Table I in most cases. However, the accuracy will be low in regions where the slope of the (E, y_0) curve is small.

In order to find out how the E.M. depends on the mobilities of the small ions, we carried out a few calculations with $m_+ \neq 0.184$ and/or $m_- \neq 0.184$ (cf. Eq. [28]). Most of the results are given in Table II. The values $m_{\pm} = 0.0655$ and $m_{\pm} = 0.0368$ correspond to limiting equivalent conductances of 196 and 350 ohm^{-1} cm.^{2} eq.$^{-1}$, respectively, in aqueous solutions at 25°C. (under these circumstances, the values for OH$^-$ and H$^+$ are 197 and 350, respectively). Relevant data for $m_{\pm} = 0.184$, taken from Table I, are given in the third column of Table II.

From inspection of these results it follows that E depends linearly on m_+ and m_-, and that, when both m_+ and m_- differ from 0.184, the corrections may be linearly superimposed. These conclusions are valid for the intervals $0.0368 \leq m_{\pm} \leq 0.184$. They are
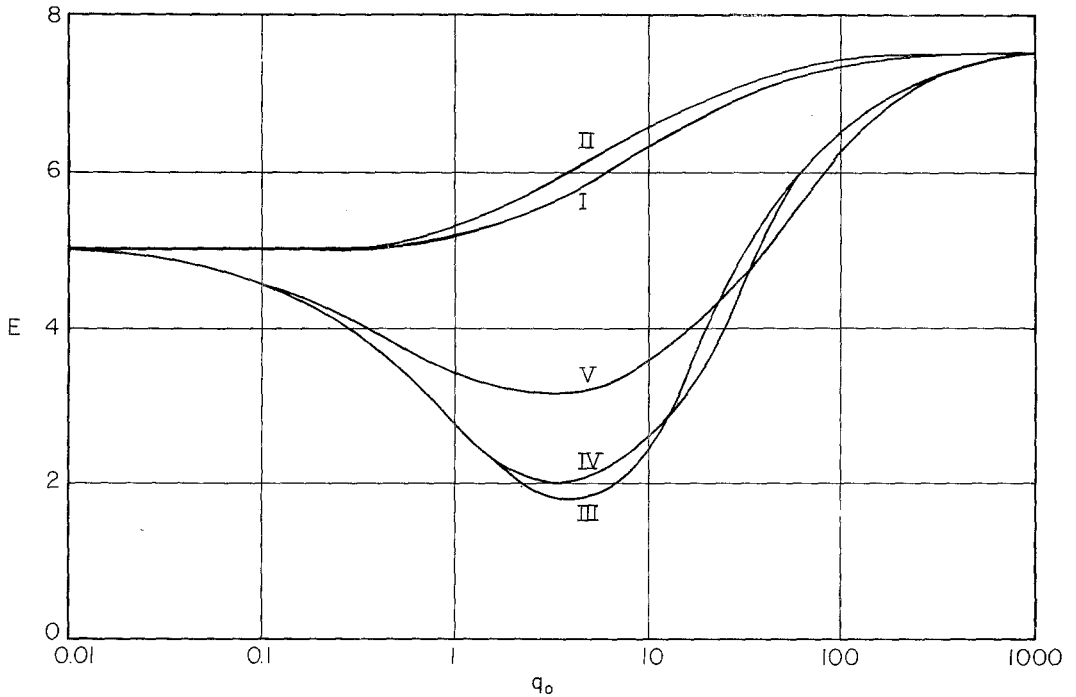
FIG. 4. E as a function of q_0 for $z_+ = z_- = 1$, $y_0 = 5$, $m_+ = m_- = 0.184$. I: Eq. [33] (Henry); II: first approximation of numerical computations; III: Eq. [34] (Overbeek); IV: Eq. [36] (Booth); V: numerical computations.

TABLE II

VARIATION OF E WITH m_+ AND m_- FOR
A FEW COMBINATIONS OF y_0 AND q_0
(1-1 ELECTROLYTES)

q_0	y_0	$m_+ = 0.184$ $m_- = 0.184$	0.0655 0.184	0.0368 0.184	0.184 0.0655	0.184 0.0368	0.0368 0.0368
				E			
0.1	3	2.904	2.921	2.926	2.927	2.936	
0.1	5	4.585	4.652	4.668	4.693	4.719	4.807
1	3	2.625	2.657	2.663	2.693	2.710	2.746
1	5	3.436	3.506	3.523	3.648	3.704	3.792
2	5	3.199				3.463	
5	3	2.742	2.771	2.775	2.833	2.857	2.890
5	5	3.169	3.214	3.225	3.402	3.463	3.533
10	5	3.470				3.813	
20	5	4.098				4.476	
50	3	3.921	3.932	3.937	3.976	3.990	4.004
50	5	5.250	5.270	5.275	5.531	5.591	5.622

supported by the analytical approximations [34] and [36].

A more detailed calculation, including higher values of m_+ and m_-, was carried out

for only one combination of q_0 and y_0, viz., $q_0 = 10$, $y_0 = 5$. The results are shown in Fig. 5. The highest values of m_+ and m_- ($m_\pm = 0.74$) correspond to the limiting equivalent conductance of the lauryl sulfate ion (17 ohm^{-1} cm.^{2} eq.$^{-1}$) in aqueous solution at 25°C. In the larger region considered here, E depends linearly on m_+, but not on m_-. When both m_+ and m_- differ from 0.184, the two corrections may be superimposed even for larger values of m_+ and m_-. Further detailed computations on the relation between E and m_- (i.e., for other combinations of q_0 and y_0) would have consumed too much computer time. Extrapolation of the data of Table II will lead to significant errors only when the counter-ion is very slow. We shall return to this matter in Part E.

Values of $\partial E/\partial m_\pm$, computed from Table II with the assumption of linear dependence, are given in Table III. These results show that E always decreases with increasing m_+ and m_-, i.e., with increasing friction factors of the small ions. This can also be

expressed by stating that the slower ions give the larger relaxation effect. This could be expected, because the time of relaxation increases with decreasing ionic mobility.

The application of mobility corrections to practical cases will be discussed in Part E.

D. THE EFFECT OF BROWNIAN MOVEMENT

The more recent theories (13, 14) of electrolytic conductance take into account that the so-called central ion, by its own thermal motion, takes part in the relaxation of its ionic atmosphere. When the central ion is a colloid particle, the Brownian motion of this particle has a similar effect, which was not considered in the computations reported in Tables I and II. However, for 1-1 electrolytes the upper limit of the Brownian motion correction was calculated approximately (7a); in these special calculations, the values of m_+ and m_- were chosen equal to 0.184. The numerical results, which are given in reference 7b, will not be repeated here in detail; they can be represented with good accuracy by Eq. [37]:

$$0 < \Delta E' < \alpha y_0^3 \frac{f_\pm}{f_\pm + 6\pi\eta a}. \qquad [37]$$

In this equation, $\Delta E'$ is the Brownian motion correction to the E.M., expressed in dimensionless units (cf. Eq. [22]); $f_\pm$ are the friction coefficients of the small ions (these coefficients were assumed to be equal); $6\pi\eta a$ is the friction coefficient of the colloid particle; α is a function of q_0, of which the following values are known: $q_0 = 0$, $\alpha = 0$; $q_0 = 0.1$, $\alpha = 0.004$; $q_0 = 1$, $\alpha = 0.018$; $q_0 = 5$, $\alpha = 0.030$. It follows that the correction is positive, as was to be expected. It should be observed that a large value of q_0 ($\equiv \kappa a/\lambda$) implies either a large value of a or a large ionic strength. In the first case, the correction is small because of the a in the denominator of Eq. [37]; the latter case is unlikely to occur in stable colloid systems, or is, at any rate, inconsistent with a high ζ-potential (i.e., a high value of y_0). This argument explains why the region $q_0 > 5$ was not considered in these computations; it also leads to the conclusion that $\Delta E'$ is negligible in most practical cases. In addition, there is another small effect which leads to a negative correction to the E.M. At finite concentrations of the small ions, these ions themselves are retarded by their own atmospheres (electrophoretic retardation + relaxation effect). In recent treat-
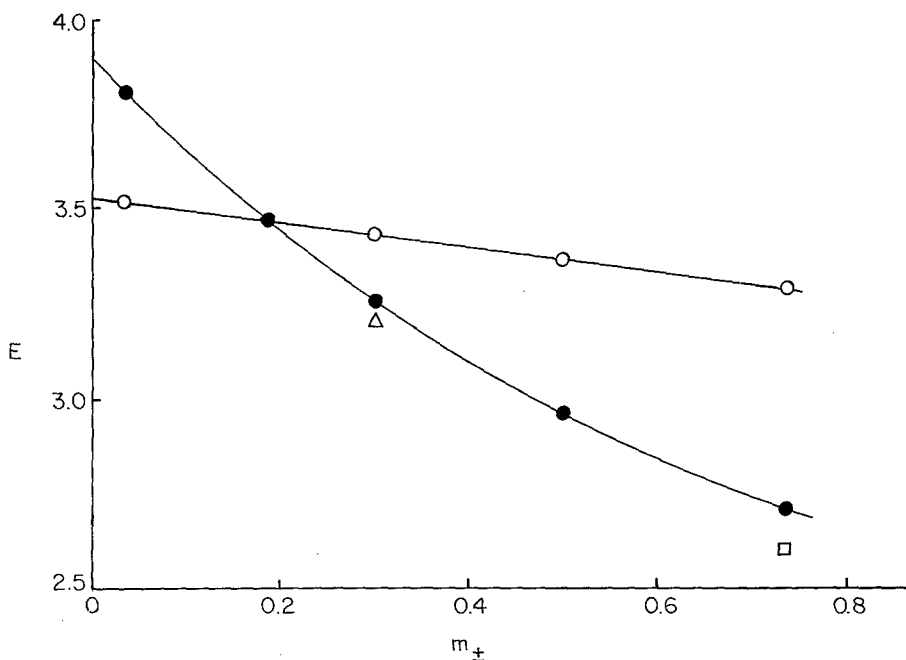

FIG. 5. $\bigcirc$: E vs. m_+ ($m_- = 0.184$); $\bullet$: E vs. m_- ($m_+ = 0.184$); $\triangle$: $m_+ = m_- = 0.3$; $\square$: $m_+ = m_- = 0.74$.

TABLE III

$\partial E/\partial m_+$ AND $\partial E/\partial m_-$ AS FUNCTIONS OF q_0 AND y_0 FOR UNIVALENT ELECTROLYTES

y_0	$-\partial E/\partial m_+$				$-\partial E/\partial m_-$						
	$q_0 = 0.1$	1	5	50	$q_0 = 0.1$	1	2	5	10	20	50
3	0.15	0.27	0.26	0.10	0.21	0.58		0.78			0.47
5	0.56	0.59	0.38	0.17	0.91	1.80	1.79	1.98	2.33	2.57	2.34

TABLE IV

E AS A FUNCTION OF q_0 AND y_0 FOR 2–2 ELECTROLYTES AND FOR FOUR TYPES OF UNSYMMETRICAL ELECTROLYTES

	y_0	$q_0 = 0.1$	0.2	1	5	20	50
$z_+ = z_- = 2$	1	0.991	0.984	0.968	1.059	1.267	1.402
$m_+ = m_- = 0.368$	1.5				1.417		
	2	1.924	1.865	1.637	1.619	2.056	2.456
	2.5		2.246	1.826	1.693	2.176	2.737
	2.75					2.164	
	3	2.798	2.601	1.943		2.124	2.800
$z_+ = 2; z_- = 1$	1				1.191		
$m_+ = 0.368$	2	2.011	2.009	2.021	2.222	2.604	2.802
$m_- = 0.184$	2.75				2.79		
	3	2.971	2.933	2.78		3.58	4.009
	4	3.835					
$z_+ = 3; z_- = 1$	1	1.022	1.032	1.088	1.231	1.385	1.445
$m_+ = 0.552$	1.75				2.064	2.352	
$m_- = 0.184$	2	2.042	2.049	2.09			2.824
$z_+ = 1; z_- = 2$	1	0.979	0.970	0.931	1.004	1.224	1.356
$m_+ = 0.184$	2	1.887	1.821	1.547	1.495	1.948	2.377
$m_- = 0.368$	2.5		2.177	1.719	1.545	2.034	2.628
	2.75				1.541		
	3	2.738	2.479	1.824		1.951	2.656
$z_+ = 1; z_- = 3$	1	0.961	0.941	0.849	0.870	1.104	1.281
$m_+ = 0.184$	$1\tfrac{2}{3}$			1.139	1.011	1.339	1.744
$m_- = 0.552$	2	1.827	1.661	1.208	0.992	1.278	1.772

ments of electrolytic conductance (14), this effect is accounted for; it is neglected if one computes the parameters $m_\pm$ (cf. Eq. [30]) from the limiting equivalent conductances, $\lambda_\pm^0$, of the small ions. This effect can be included by using $\lambda_\pm(c)$ (the equivalent conductances at the given small ion concentration) instead of $\lambda_\pm^0$. A few calculations (7a) which were carried out using the data of Tables II and III have shown that this effect cancels the Brownian motion correction to a large extent. Therefore, in practical applications, the best one can do at present is to neglect $\Delta E'$ (because only an upper limit of this correction is known) and to use $\lambda_\pm^0$, not $\lambda_\pm(c)$, in Eq. [30].

E. OTHER TYPES OF ELECTROLYTE

Additional types of electrolyte that have been considered are: 2-2, 2-1, 3-1, 1-2, and 1-3 (2-1 indicates that the positive ion is bivalent and the negative ion is monovalent, etc.). The results are given in Table IV. In all these computations, the values of m_+ and m_- were chosen equal to $0.184\, z_+$ and $0.184\, z_-$, respectively. Therefore, all data apply to ionic mobilities of 70 ohm^{-1} cm.^{2} eq.$^{-1}$ at 25°C. in aqueous solutions (cf. Eq. [30]).

It should be noted that the data apply to a positive colloid particle. In practical cases where the colloid is negative, the numerical data for 1-2 electrolytes should be used when the actual electrolyte is $Ba(NO_3)_2$, etc.

Because of convergence problems, the results reported in this section are limited to rather low values of y_0. The variation of E with m_+ and m_-, and the Brownian motion correction, have not been considered, because only a limited amount of computer time was available.

For 2-2 electrolytes, the numerical results and the differences between numerical and approximated values follow the same pattern as those for univalent electrolytes.

In Figs. 6 and 7, some data for different valence types of electrolytes are compared. The effect of z_-, the valence of the counterions, is represented in Fig. 6. The values of

E are plotted against $q_0' \equiv q_0(z_+/z_-)^{1/2}$ instead of against q_0. This is done because q_0 is proportional to $(cz_-)^{1/2}$ (cf. Eq. [26]), with the result that variation of z_- produces a trivial variation of the coordinate q_0. The variable q_0' is proportional to $(cz_+)^{1/2}$. Therefore, all data for a given q_0' and different values of z_- (e.g., KCl and K_2SO_4) correspond to the same equivalent concentration, c, and can be conveniently compared. In Fig. 7, which represents the effect of z_+, q_0 is used because in this case q_0 is constant for constant c, even if z_+ changes.

Comparison of Figs. 6 and 7 shows that the valence of the counter-ions has much more effect on the E.M. than has the valence of the co-ions. The curves labeled IV in Figs. 6 and 7 correspond to zero relaxation effect. It follows that multivalent counterions give a negative relaxation effect which
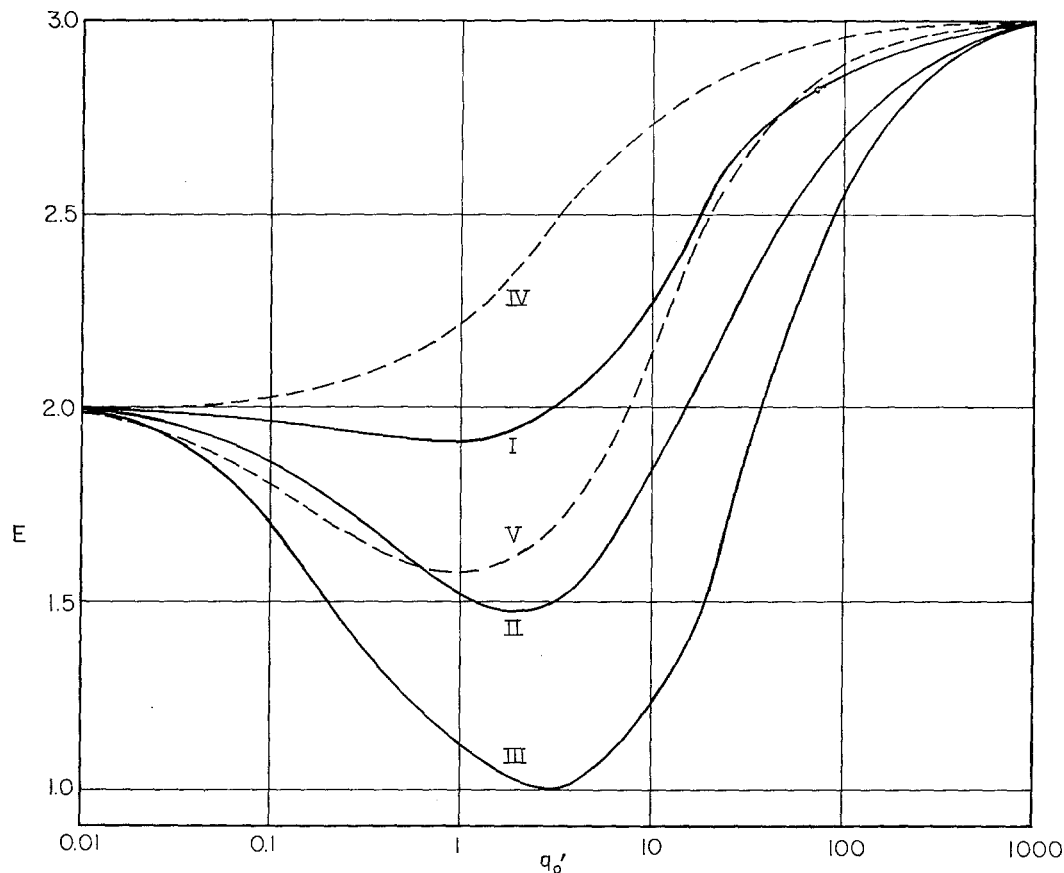

FIG. 6. Effect of valence of counter-ions on the E.M.; $y_0 = 2$. Drawn lines: numerical values (I: $z_+ = z_- = 1$; II: $z_+ = 1$, $z_- = 2$; III: $z_+ = 1$, $z_- = 3$). Dotted lines: approximations for $z_+ = 1$, $z_- = 3$ (IV: first approximation of numerical computations; V: Eq. [35] (Overbeek)).
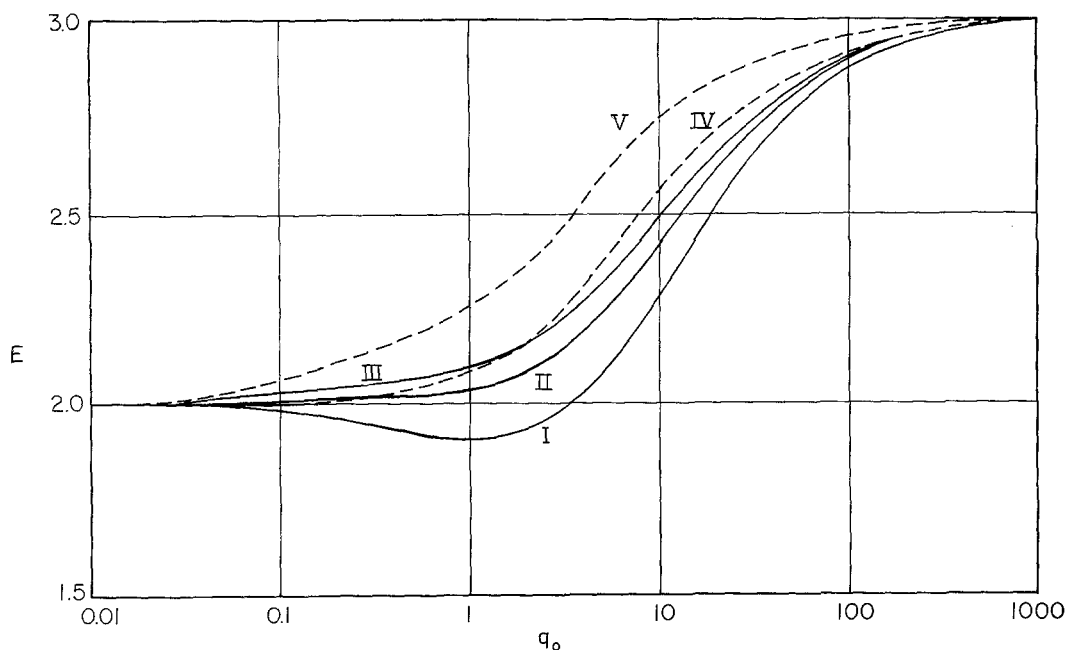
FIG. 7. Effect of valence of co-ions on the E.M.; $y_0 = 2$. Drawn lines: numerical values (I: $z_+ = z_- = 1$; II: $z_+ = 2$, $z_- = 1$; III: $z_+ = 3$, $z_- = 1$). Dotted lines: approximations for $z_+ = 3$, $z_- = 1$ (IV: first approximation of numerical computations; V: Eq. [35] (Overbeek)).

increases in absolute value with the valence of the counter-ions. For multivalent co-ions, most of the data show a negative relaxation effect which decreases in absolute value with increasing valence of these ions; the relaxation effect is positive for 3-1 electrolytes and $0.01 < q_0 < 1$. A positive relaxation effect was also predicted by Overbeek, but according to the computer results it is less pronounced. Finally, we recall that, for univalent electrolytes and $y_0 = 2$, Overbeek's equation [34] gives practically the same results as do our computations. It follows that Eq. [34] is a much better approximation than is Eq. [35]. This was to be expected, because the coefficient of y_0^3 in Eq. [35] is incomplete, as was mentioned by Overbeek (5b).

F. APPLICATIONS TO PRACTICAL CASES

We shall now discuss the calculation of ζ-potentials from E.M. measurements. The discussion applies especially to univalent electrolytes; at the end of this Part we shall indicate to what extent it can be generalized to other valence types.

Suppose that a set of experimental values

of the electrophoretic mobility, U/X, has been obtained and that the radius, a, of the particles is known. Then the mobility values should be converted to the dimensionless quantity E (Eq. [22]). We shall give two examples (aqueous solutions at 20°C. and 25°C.), using the following numerical values:

$e = 4.803 \times 10^{-10}$ e.s.u.

$\eta_{20} = 0.01005$ poise.

$\eta_{25} = 0.008937$ poise.

$\epsilon_{20} = 80.36$.

$\epsilon_{25} = 78.54$.

$k = 1.3805 \times 10^{-16}$ erg deg.$^{-1}$.

$0° = 273.16°$K.

When the mobility, U/X, is expressed in cm.^{2} volt^{-1} sec.$^{-1}$,

$$E = 0.8387 \times 10^4 (U/X) \text{ at } 20°C. \quad [38]$$

$$E = 0.7503 \times 10^4 (U/X) \text{ at } 25°C. \quad [39]$$

Next, the value of q_0 should be computed from the particle radius and the properties of the surrounding electrolyte. From Eq. [26], if we use $N_a = 6.0226 \times 10^{23}$ and the numerical values already listed:

$$q_0 = (0.3279 \times 10^8)(cz_-)^{1/2}a \text{ at } 20°C.; \quad [40]$$

$$q_0 = (0.3286 \times 10^8)(cz_-)^{1/2}a \text{ at } 25°C. \quad [41]$$

Here c = concentration in equivalents per 1000 cm.^{3} aqueous solution.

At this stage it is advisable to decide whether some analytical approximation can be used. First, one should inspect Fig. 2 and check whether the experimental combination (E, q_0) lies within a region where E does not depend on q_0. If this is the case, one may use either Eq. [31] ($q_0 \gg 1$) or [32] ($q_0 \ll 1$). If not, the next step is to find out whether Henry's approximation (Eq. [33]) is valid. This can be done by inspection of Fig. 8. For combinations of E and q_0 which lie above the drawn line (labeled I), Eq. [33] will lead to an error of more than 1 mv. in the ζ-potential; for combinations (E, q_0) lying above the dotted line (II), the error will exceed 2.5 mv. In this context, an error means a difference between two values of ζ calculated by means of Eq. [33] and by means of the computer results. The lines of Fig. 8 apply to $m_+ = m_- = 0.184$ ($\lambda_{\pm}^0 = 70$ ohm^{-1} cm.^{2} eq.$^{-1}$); for slower ions (especially slower counter-ions), the lines would shift to slightly lower values of E.

If it is found that Eq. [33] is not sufficiently accurate, the values of m_+ and m_-

must be calculated from the limiting mobilities, $\lambda_{\pm}^0$, of the small ions. Using Eq. [30] and the listed numerical values, we find:

$$m_{\pm} = 11.51 \frac{z_{\pm}}{\lambda_{\pm}^0} \quad \text{at} \quad 20°\text{C.}; \qquad [42]$$

$$m_{\pm} = 12.86 \frac{z_{\pm}}{\lambda_{\pm}^0} \quad \text{at} \quad 25°\text{C.} \qquad [43]$$

Here $\lambda_{\pm}^0$ are given in ohm^{-1} cm.^{2} eq.$^{-1}$. When a mixture of univalent electrolytes is present, m_+ and m_- may be calculated from the number averages of λ_+^0 and λ_-^0; this approximation is not based upon the theory, but the error will be small because of the small effect of $m_{\pm}$ on the E.M.

The next step is to decide whether Overbeek's approximation (Eq. [34]) can be used. This can be done by means of Fig. 8. The drawn line (III) corresponds to an error of 1 mv. in the ζ-potential, the dotted line (IV) to an error of 2.5 mv. These lines do not shift appreciably when λ_+^0 and/or λ_-^0 differ from 70 ohm^{-1} cm.^{2} eq.$^{-1}$, because the effect of $\lambda_{\pm}^0$ is included in Eq. [34] as well as in our computation. If it is found that Eq. [34] can be used, it is preferable to
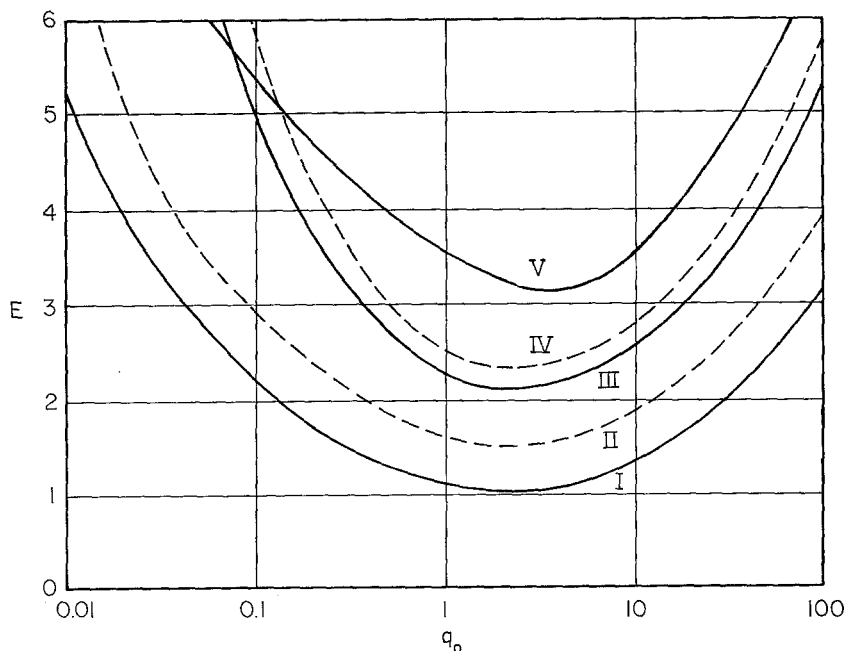

FIG. 8. Errors of analytical approximations. I and II: Eq. [33] (Henry); III and IV: Eq. [34] (Overbeek); V: limitations of computer results. For further explanation see text.

do so, because the calculation of ζ by means of the present numerical data is somewhat more time-consuming.

When our numerical data must be used, one may proceed as follows. First, several curves of E vs. q_0 are constructed from the data of Table I (*cf.* Fig. 2). Next, from these curves a set of values of E is derived for the value of q_0 which follows from the experimental data. These values of E apply to $m_+ = m_- = 0.184$ and must be corrected if necessary.

This correction can be found from the data of Part C; it should be observed that these data apply to a positive colloid particle. It is best to assume that E varies linearly with m_+ and m_- and to use the data of Table III, because no detailed curves of E vs. m_+ and m_- are available. As was mentioned in Part C, this will lead to significant errors only when the counter-ion is very slow. (An additional correction for that case will be suggested below.) The required values of $\partial E/\partial m_{\pm}$ can be found by interpolation from Table III. First, $\partial E/\partial m_+$ and $\partial E/\partial m_-$ are plotted against q_0 for $y_0 = 3$ and $y_0 = 5$. From these plots one obtains the differential quotients for the proper value of q_0 and for two values of y_0. Next, $\partial E/\partial m_+$ and $\partial E/\partial m_-$ are plotted against y_0. In constructing these plots it should be observed that $\partial E/\partial m_{\pm} = 0$ for $y_0 = 0$, and that $\partial/\partial y_0(\partial E/\partial m_{\pm}) = 0$ for $y_0 = 0$, as can be concluded from Eqs. [34] and [36]. Even then, these graphs will not be very accurate, but this is not serious, because we are dealing with small corrections. From these plots one obtains, for every value of y_0, the total correction, ΔE, according to the equation

$$\Delta E = (m_+ - 0.184) \frac{\partial E}{\partial m_+}$$
$$+ (m_- - 0.184) \frac{\partial E}{\partial m_-}. \qquad [44]$$

The algebraic values of ΔE must be added to the values of E that were obtained for $m_{\pm} = 0.184$. For very slow counter-ions, it is advisable to correct the value of $\partial E/\partial m_-$; the correction can be estimated by assuming that, for all combinations of q_0 and y_0, the

curvature of the (E, m_-)-plot is the same as in Fig. 5.

Finally, the corrected values of E are plotted against y_0. From this graph one finds y_0, using the value of E that follows from experiment. Because $y_0 = e\zeta/kT$, ζ is found from the equations

$$\zeta = 25.26 \, y_0 \text{ mv. at } 20°C. \qquad [45]$$

$$\zeta = 25.69 \, y_0 \text{ mv. at } 25°C. \qquad [46]$$

At this point we wish to mention that the upper drawn line in Fig. 8 shows the limitations of the computer results for 1-1 electrolytes. If an electrophoresis experiment implies a combination of E and q_0 (e.g., $q_0 = 5$, $E = 4$) which lies above this line, it is not possible to calculate a ζ-potential from the computer data, either because the computations were not carried through far enough (i.e., for $y_0 \leqq 6$ only) or because the E, y_0 curve shows a maximum.

The surface charge density, σ, can be obtained using the data given in references 7 and 9, where the relation between σ and ζ is given in tabulated form. In the context of electrophoresis, σ is defined by observing that $4\pi a^2\sigma$ is the charge contained within a sphere of radius a, where a is the distance between the center of the particle and the slipping plane.

We shall now indicate briefly how much of the preceding discussion can be applied to nonunivalent electrolytes. The numerical data for these valence types are rather incomplete and are therefore less suitable for accurate calculations of ζ.

The equations of this Part (except for Eq. [44]) are valid for any valence type. Hence, the calculations of E and q_0 are straightforward. However, in comparing computer data with analytical approximations, one should remember that q_0 equals $\kappa a/\lambda$ not κa.

For 2-2 electrolytes, the approximations of Henry and of Overbeek break down at much lower values of y_0 (and of E) than they do for 1-1 electrolytes. This also applies to unsymmetrical electrolytes when the counter-ions are multivalent (*cf.* Fig. 6). When the co-ions are multivalent, the situation is different (Fig. 7). In this case, Henry's approximation is better for 2-1

and 3-1 electrolytes than it is for the 1-1 type, and it also happens to be more accurate than Eq. [35] of Overbeek.

Because the variation of E with m_+ and m_- was not computed for nonunivalent types, it can only be estimated with the aid of the analytical approximations. According to Overbeek's equation [34] for symmetrical electrolytes, $\partial E/\partial m_+$ and $\partial E/\partial m_-$ do not depend on z_+ and z_- (the valences enter into the relations between $m_\pm$ and $\lambda_\pm{}^0$, Eqs. [42] and [43]). Hence, for 2-2 electrolytes it seems reasonable to calculate $\partial E/\partial m_\pm$ from Table III and to compute the mobility correction from Eq. [44], replacing 0.184 by 0.368. This correction can then be applied to the values of E found from Table IV.

A similar procedure can be applied to unsymmetrical electrolytes, taking into account that, for this case, Overbeek's Eq. [35] predicts that $\partial E/\partial m_\pm$ is proportional to $z_\pm/(z_+ + z_-)$. For example, for a 1-3 electrolyte (positive colloid), the value of $\partial E/\partial m_-$, computed from Table III, should be multiplied by a factor of $(3/4)/(1/2) = 3/2$; the result should be inserted into Eq. [44], replacing $(m_- - 0.184)$ by $(m_- - 0.552)$.

Numerical data concerning the relation between σ and ζ for unsymmetrical electrolytes can be found in reference 9.

G. COMPARISON OF THEORY AND EXPERIMENT

The theoretical computations predict a relation between the E.M. and the ζ-potential. Of these two, the E.M. can be measured directly, whereas the ζ-potential (or changes of ζ) cannot. This makes it rather difficult to find a really quantitative experimental test.

Following an indirect approach, one may try to find the ζ-potential from other experiments, such as electroosmosis, streaming potential, determination of electrocapillary curves, and titration. Although it is possible to obtain additional information in this way, this discussion will be limited to measurements of the E.M. itself.

Before quoting examples from the literature, we shall discuss some requirements that should preferably be met by a suitable experiment. Some of the assumptions under-

lying the present computations can be satisfied by the choice of the experimental system. It is desirable that the colloid particles be rigid, impenetrable to the surrounding solution, spherical, and nonconducting. The colloid concentration should be sufficiently low to avoid overlapping of ionic atmospheres. Mixtures of different valence types should be avoided. Important parameters, such as κa, must be well defined; this excludes experiments with particles of unknown size or a wide size distribution.

Furthermore, it is desirable that certain parameters can be varied independently. This requirement causes a few problems. When the surface potential of the particle is changed by varying the concentration of the potential-determining ions, the value of κa may also change. This problem is not serious because it can either be avoided (by using a relatively high concentration of indifferent electrolyte) or be taken into account in the calculation of κa. The variation of κa is more difficult. When this is done by changing the ionic strength, the ζ-potential may also change and a correction for this important side effect requires additional theoretical assumptions. Therefore, a better way of varying κa is to work with different monodisperse colloidal solutions of varying particle size.

Of the many electrophoresis experiments that were reported in the literature, very few (15–17) were carried out systematically with the purpose of testing the more recent theories. The other examples that will be quoted were chosen according to the points of view given above, with a preference for cases in which the relaxation effect is appreciable. Only examples with 1-1 electrolytes were considered because the present theory for other valence types is rather incomplete. The E.M. values were converted to the dimensionless variable E, in order to account for differences in temperature and to facilitate the use of data (such as Fig. 8) given previously in this paper.

The more important parameters in the theory are ζ and κa. We shall first consider measurements of the E.M. as a function of the concentration of potential-determining ions. This method of testing the theory is rather limited because it is not known quan-

TABLE V

COMPARISON OF EXPERIMENTAL AND THEORETICAL MAXIMUM VALUES OF THE ELECTROPHORETIC MOBILITY OF SILVER HALIDE SOLS

Sol	Ref.	Added electrolyte	$\varkappa a$	$E_{max}.$ (expt.)	$|E_{max}.|$ (theor.)
AgBr	19	—	13	$+3.41$	3.72
AgBr	20	2.5 mmoles KNO$_3$	16.5	$+3.23$ -3.60	3.92
AgI	21	12 mmoles KNO$_3$	11	$+3.6$ -4.5	3.60
AgI	22	—	4–5	$+2.86$ -3.14	3.14–3.17
AgI	23	—	1.23	$9+3.4$	3.6

titatively how ζ changes with the surface potential, ψ_0. However, one important feature of the theory can be tested rather effectively in this way. The data of Table I predict that, for intermediate values of $\varkappa a$, the E.M. does not exceed certain maximum (or limiting) values, whatever the value of ζ may be. Hence, it is of interest to find out whether mobilities have been observed that do exceed these theoretical limits.

Most inorganic colloids do not show very high mobilities. Holliday (18) reports a value for a stable gold sol, which gives $E = 3.26$ at $\varkappa a = 0.833$. A number of experiments on silver halide sols are summarized in Table V. In all these experiments, the E.M. was measured as a function of p_{Ag}. Only maximum values are quoted; the theoretical results apply to $m_+ = m_- = 0.184$, but the mobility corrections are small, especially when most of the ions are K$^+$ and NO$_3{}^-$. The value $E = -4.5$ found by Troelstra (21) exceeds the maximum ($|E| = 3.6$) that follows from the present theory. The data for $\varkappa a = 4$–5 are part of a complete curve of the E.M. vs. p_{Ag}, which was measured by Parfitt and Smith (22). The E.M. values, which were kindly sent to the authors by Dr. Parfitt, show a maximum ($E = -3.14$) that exceeds the theoretical limit for $\varkappa a = 4$ and just coincides with the limit for $\varkappa a = 5$. (The values of ζ, computed from this curve by means of the present theory, definitely pass through a maximum as p_I decreases. This detail is mentioned here because a maximum in the ζ-potential is

considered by Levine and Bell (24) as a support of the theory of the discreteness-of-charge effect.)

The silver halide sols are not entirely suitable for testing, because the particles are not spherical. This condition is more nearly satisfied by certain soap micelles. Stigter and Mysels (25) measured the E.M. of sodium lauryl sulfate micelles as a function of soap concentration and ionic strength. They extrapolated to the CMC as the E.M. was found to decrease with increasing micelle concentration. The extrapolated values, converted to E, are given in Table VI as a function of $\varkappa a$. The third column of this table gives the corresponding maxima predicted by the theory of Overbeek. The next column shows the values of E (for $y_0 = 6$, i.e., $\zeta = 150$ mv.) that follow from the present theory. The latter data are not maxima or limits, but the end points of ascending theoretical curves (no computations for $y_0 > 6$). The values in columns 3 and 4 were corrected for the small ion mobilities of the Na$^+$ and lauryl sulfate ions that are present in the system. All experi-

TABLE VI

MOBILITY AND ζ-POTENTIAL OF SOAP MICELLES

$\varkappa a$	E (expt.)	$E_{max}.$ (Overbeek)	E (present theory, $y_0 = 6$)	ζ (mV) Stigter and Mysels	ζ (mV) Present theory
0.61	3.41	2.53	3.37	101	162
0.86	3.20	2.80	3.46	92.3	116
1.32	2.88	2.64	3.27	80.9	97.4
1.69	2.72	2.56	3.15	75.0	90.5
2.40	2.57	2.50	3.01	68.3	80.7

TABLE VII

MOBILITY OF POLYSTYRENE LATICES

Latex	$\varkappa a$	$|E|$ (expt. limiting values) Dialyzed	$|E|$ (expt. limiting values) Undialyzed	$|E_{max}.|$ (theor.)
A	2.22	2.13	2.40	3.09
B	3.80	2.22		3.01
C	8.93	2.59	3.08	3.28
D	13.6	3.56		3.55
E	15.6	3.80	4.11	3.68

mental values exceed the maxima predicted by Overbeek and by Booth. In the last two columns of Table VI, the values of ζ published by Stigter and Mysels (25) are compared with those computed from the present theory (the first value in the last column was found by a short extrapolation of the theoretical curve). The differences between the two sets of values are appreciable, but they do not seem to invalidate the conclusions drawn by Stigter and Mysels from their experiments. The interpretation of these experiments has been recently discussed again by Stigter (26).

Rather high mobilities are also found in polymer latices. This can be concluded from papers by Maron and co-workers (27), Voyutsky and Panich (28), and Sieglaff and Mazur (29). These data are not suitable for a quantitative comparison with theory, because 1-2 electrolytes (Na_2HPO_4-buffer) are present in the system (27), temperature and $\varkappa a$-value are not reported (28), or the values of $\varkappa a$ are too high (29) to obtain an appreciable relaxation effect. Recently, systematic E.M. measurements on monodisperse polystyrene latices of five different particle sizes were carried out by Shaw and Ottewill (30), who very kindly permitted us to quote from their results. The polystyrene particles are charged by built-in COOH groups and by adsorbed lauric acid. The E.M. of the particles increases with increasing pH until a limiting value is reached at a pH of about 7. The limiting values, measured at pH = 7.6 and 25°C. in 5×10^{-4} M NaCl, are given in Table VII (dimensionless units). The values given in the third column of this table were measured after the latices had been dialyzed exhaustively; in these cases, no lauric acid was present in the system. The last column of Table VII gives the maximum values of E predicted by the present theory (corrections for the mobilities of the small ions have been included). The values of the E.M. measured in latex E are significantly higher than the predicted maximum.

From the preceding discussion it follows that experimental mobilities exceeding the theoretical limits are rather exceptional, and that the differences are relatively small.

Next, we shall consider some experiments in which the E.M. was measured as a function of particle size, at constant composition of the medium surrounding the particles. As indicated above, this is the best way of checking the theoretical relation between the E.M. and $\varkappa a$.

Systematic measurements of this type were carried out by Kemp (16) on sols of gamboge and silica, with the purpose to test the theory of Henry (4). Because the mobilities are rather low, the results are not suitable for testing the present theory. Next, we come to experiments of Mooney (15), Jordan and Taylor (31), and von Stackelberg and Heindze (17). All these authors have used emulsions; there is some doubt as to whether emulsion droplets behave as rigid particles, but recent publications are reassuring on this point. Anderson (32) measured the E.M. of n-octadecane dispersions at a series of temperatures above and below its melting point and did not find any discontinuity. From experiments on drops rising or falling in water, Linton and Sutherland (33) conclude that inside circulation occurs only in large droplets consisting of polar oils, and that small impurities (surfactants) at the interface are sufficient to stop this circulation. Mooney (15) has reported some very high mobilities; e.g., in his Fig. 4, $E = 7.5$ at $\varkappa a = 33$, assuming a temperature of 25°C. This value of E is much higher than the theoretical maximum for this $\varkappa a$ (cf. Fig. 8), but this might be due to inner circulation, for the oils used by Mooney are polar and no stabilizers are mentioned. For this reason, and because no temperatures are reported, no quantitative conclusions will be drawn from this work; qualitatively, the dependence of the E.M. on particle size is consistent with the theory of the relaxation effect. Jordan and Taylor (31) measured the mobilities of decaline drops for two different sizes ($\varkappa a = 2.7$ and $\varkappa a = 136$). The mobility ratio was found to be in reasonable quantitative agreement with Overbeek's theory. Because ζ is not large in this case (ca. 100 mv.) the difference between Overbeek's theory and the computer results does not exceed 10 % at $\varkappa a = 2.7$ and is negligible at $\varkappa a = 136$. The detailed investigation by

von Stackelberg and Heindze (17) was carried out with the purpose of testing the theories of Overbeek and of Booth. The authors conclude that theory and experiment are in good qualitative agreement. Because $\zeta < 100$ mv. and $\kappa a > 10$ in these experiments, they also confirm the present theory, which gives about the same results for these parameter combinations. Similar conclusions can be drawn from the measurements of Shaw and Ottewill (30) on polystyrene latices. These authors report that the E.M. values for latices A, B, and C, measured in 5×10^{-5} M NaCl, exhibit a minimum when plotted against κa; this minimum occurs in the region $1 < \kappa a < 2$, in agreement with the theoretical prediction.

H. Conclusions

From the preceding literature review it can be safely concluded that the theory presented in this paper is qualitatively correct. Furthermore, some critical experiments (silver halide sols, soap micelles) show that the present theory explains more facts than do the preceding theories. However, a few experiments on AgI sols (21, 23) and, especially, certain high mobilities by Shaw and Ottewill (30) in polystyrene latices indicate that our calculated mobilities are probably somewhat low. This implies that one or more assumptions used in the theory are not quite correct. A few possibilities will now be considered briefly.

In the present model it is assumed that ϵ and η have bulk values in the region outside the slipping plane. These assumptions were examined by Lyklema and Overbeek (34). The authors found that the correction for decreased values of ϵ in the double layer is mostly negligible. It was estimated that the correction for increased viscosity (the viscoelectric effect) might be appreciable (i.e., 20% at high ζ and high ionic concentration). However, there are indications that the viscoelectric effect is overestimated by Lyklema and Overbeek, as has been pointed out recently by Stigter (35).

It has already been mentioned that, as far as the region outside the slipping plane is concerned, surface conductance is included in our model. A surface conductance

within the slipping plane was not accounted for, but this is not likely to occur, because the ions in this region are probably at least as firmly bound to the surface as are the molecules of the solvent.

If the corrections mentioned so far were taken into account, they would lead to lower theoretical mobilities. Since our model, as it is, already leads to low theoretical values, we still need a positive correction in order to explain the discrepancies between theory and experiment. The Brownian motion correction is positive indeed, but it is far too small to account for the differences.

Another source of error might be the assumption of a continuous surface charge. The discreteness-of-charge effect certainly changes the relation between ψ_0 and ζ, and therefore the mobility at a given ψ_0. From a recent paper by Levine and Bell (24), however, it seems correct to conclude that this effect is mostly confined to the inner regions of the double layer, with the result that the relation between ζ and the E.M. is not affected.

Finally, there are several objections against the use of the classical Gouy-Chapman theory. La Mer (36) recently expressed the view that the use of the complete Poisson-Boltzmann equation is fundamentally incorrect for large colloidal particles, and that a more advanced statistical treatment is to be preferred. Levine (37) concludes that the uncorrected Poisson-Boltzmann equation can be applied at moderate potentials (<100 mv.) and small electrolyte concentrations (<0.01 M for a univalent electrolyte). At these limits, the various corrections may already add up to 10%–20%. In our treatment of the relaxation effect, we have assumed the validity of the Poisson-Boltzmann equation in the mobile part of the double layer, up to ζ-potentials of 150 mv. It is quite possible that this assumption has led to a slight overestimation of the relaxation effect, but no definite conclusion can be drawn as long as the various corrections have not been applied to specific calculations of this effect.

For a better understanding of electrophoresis, more systematic experiments, of the type we have indicated, seem to be most

needed at this stage. If the theory is to be developed much further, it will probably be necessary to use an improved Poisson-Boltzmann equation or a new statistical treatment of the double layer. In this connection we wish to mention the work of Friedman on cluster expansions, which has been applied to equilibrium properties of strong electrolytes (38) and to electrolytic conductance (39), and a paper by Buff and Stillinger (40), who have given a new treatment of the ion and potential distribution in the double layer. It seems possible that this type of approach will be adapted to the study of nonequilibrium phenomena in colloidal systems.

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