

THE ELECTRICAL DOUBLE LAYER AND THE THEORY OF ELECTROPHORESIS

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I. THE ELECTRICAL DOUBLE LAYER

I.1 INTRODUCTION

As early as in 1809 Reuss¹ observed that in an aqueous dispersion of clay particles the latter were migrating under the influence of an applied electric field. Since that time, numerous investigations have shown this migration to be quite a general phenomenon that is displayed by colloidal particles of very diverse chemical composition and of a wide variety of sizes and shapes. It has been given the name electrophoresis. Although electrophoresis is qualitatively identical to the migration of ions in electrolyte solutions, quantitatively its description is more involved and continues to be the subject of theoretical investigations.

For practical purposes a sound theoretical foundation of electrophoresis is of considerable importance. It enables information to be obtained on the state of charge of the particles and on the hydrodynamic resistance they encounter during migration. Moreover, it predicts how electrophoretic mobilities can purposely be varied, an essential topic in separation processes.

The similarity of electrophoresis and ionic migration indicates that colloidal particles undergoing electrophoresis are electrically charged relative to the continuous medium. As to the manner in which the particles acquire their charge, four different mechanisms can be distinguished. For the above mentioned clay particles, to begin with, Si⁴⁺ ions in the crystal lattice of these compounds can be isomorphically substituted by Al³⁺ ions. This process provides them with a negative charge relative to the solution. The crystal structure of dispersed particles can also be operative in another way in the acquisition of surface charge. Several inorganic materials (e.g. the silver halides) adsorb the cations and anions that constitute their crystal lattice preferentially and usually to a different extent. Along with the ensuing surface charge, the potential difference between solid and liquid also changes in this process and therefore these ions are called *potential determining ions*. (Between a metal and a redox system, electrons play the role of potential determining ions.) In passing it may be remarked that this change in potential actually is a variation in the difference in Galvani potential between the inner core of the particles and the bulk of the solution and is not

necessarily just a surface effect. The Galvani potential difference can also vary due to other causes, such as changes in the amount and type of adsorbed dipoles. In the context of this chapter, however, only those variations that involve a redistribution of free charges (as contrasted to dipoles) will be dealt with. The third mechanism is found when surfactant ions are present in the solution. When these accumulate at the interface, as they usually do, they create a surface charge. Other ions may also be preferentially adsorbed, although usually to a lesser degree than surfactant ions. Last but not least particles may carry surface groups that can dissociate, e.g. carboxyl groups. The degree of dissociation of these groups usually depends on the pH and the composition of the solution. This fourth mechanism is particularly important for oxides, polyelectrolytes and proteins.

When the dispersed particles carry a net charge, electroneutrality of the system as a whole requires the solution surrounding them to carry a charge of the same magnitude, but with the opposite sign. The charge on the particle and that in the solution form an *electrical double layer*. The charges in solution are mobile, contrary to those on the surface. This has important consequences for the charge- (and potential-) distribution relative to the surface of the central particle. The tendency to minimize the (Coulomb) energy results in attraction of ions with a sign opposite to that of the surface (called counterions) and repulsion of ions with equal sign (co-ions). On the other hand, in order to maximize the entropy both ion types tend to reach a homogeneous distribution. When the two tendencies balance, thus when the free energy is at a minimum, the situation is very much like that in electrolyte solutions as described in the Debye-Huckel theory. An important difference with simple electrolyte solutions, however, is the circumstance that in colloidal systems the potentials can be much higher and the particles are larger, which requires a more complicated theoretical treatment.

Because all theories of electrophoresis are related to the structure of the electrical double layer around the moving entities, we start with a discussion of the latter. As a first approach only situations without an applied electrical field will be considered.

1.2 THEORY OF THE DIFFUSE DOUBLE LAYER

The theory of the diffuse electrical double layer has been developed independently by Gouy² and Chapman³. Their basic approach is very much like that of the Debye-Huckel theory, which was developed about 10 years later. Assuming all ions to be pointlike charges both theories express the combined result of electrostatic interaction and Brownian movement in terms of a Boltzmann-distribution for all ion types. This distribution can be expressed as

$$n_1 = n_{1\infty} \exp(-z_1 e \psi / kT) \quad (\text{I-1})$$

n_i is the number of ions of type i per unit volume, at a distance x from the particle surface. At this position the potential has a value ψ relative to the solution at very large x . Thus n_i and ψ are both functions of the coordinate x . $n_{i\infty}$ is the value of n_i in the bulk of the solution, where $\psi = 0$; e is the elementary charge, k the Boltzmann constant, T the absolute temperature and z_i the charge number of the ions, including their sign. Eq. (I-1) is in agreement with the statement that counterions are attracted and that co-ions are repelled. This situation is schematically depicted in fig. 1.

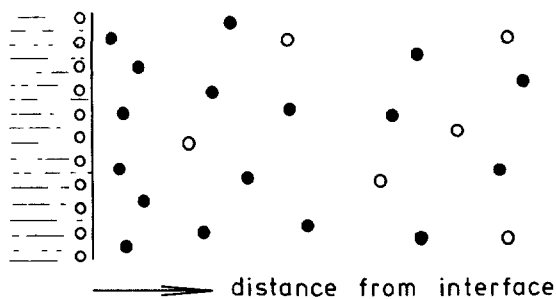


Fig. 1. Schematic distribution of negative counterions (full circles) and positive co-ions (open circles) in solution, relative to the surface of a positively charged particle (hatched area).

The net charge per unit volume of solution, the space charge density ρ , is also a function of x . It amounts to

$$\rho = \sum_i n_i z_i e \quad (\text{I-2})$$

When further elaboration of this equation is restricted to the presence of just one symmetric electrolyte ($z_+ = -z_- = z$; $n_{+\infty} = n_{-\infty} = n$), (I-2) can be written

$$\rho = ze(n_+ - n_-) \quad (\text{I-3})$$

Substitution of (I-1) in (I-3) leads to

$$\rho = -2zen \sinh(ze\psi/kT) \quad (\text{I-4})$$

which applies for every value of x . An additional relation between ψ , ρ and ψ is given by the Poisson equation. Assuming the relative dielectric constant of the solution, ϵ_r , to be independent of the field strength and applying rationalized four quantities equations this equation reads

$$\text{div}(\text{grad } \psi) = \nabla^2 \psi = - (\rho / \epsilon_r \epsilon_0) \quad (\text{I-5})$$

where ϵ_0 is the permittivity of free space ($= 8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$). Combination of (I-4) and (I-5) gives the Poisson-Boltzmann equation

$$\nabla^2 \psi = (2ze/r / \epsilon_r \epsilon_0) \sinh(ze\psi / r^m) \quad (\text{I-6})$$

which forms the basis of the Gouy-Chapman theory.

Before considering the general merits of this equation, it is worthwhile to present the approximate form of (I-6) for low potentials ($\psi \leq 25/z \text{ mV}$). In that case $\sinh(ze\psi / r^m) \approx ze\psi / r^m$ and (I-6) simplifies to

$$\nabla^2 \psi = (2r\phi^2 z^2 / \epsilon_0 \epsilon_r r^m) \psi - \kappa^2 \psi \quad (\text{I-7})$$

In passing it can be mentioned that this step is essentially the linearization used in the Debye-Hückel theory.

In the r.h.s. of (I-7) the abbreviation $\kappa^2 = (2r\phi^2 z^2 / \epsilon_0 \epsilon_r r^m)$ has been introduced. κ has the dimension of a reciprocal length. $1/\kappa$ is an important quantity that is called the Debye-length or 'the thickness of the double layer'. Whereas the physical justification of the latter term has to await the discussion of eq. (I-11), we mention here that for a mixture of electrolytes κ is defined by

$$\kappa^2 = (e^2 / \epsilon_0 \epsilon_r r^m) \sum_1 r_1 z_1^2 - \frac{2r^2 \omega}{\epsilon_0 \epsilon_r r^m} \quad (\text{I-8})$$

κ^2 is thus closely related to the ionic strength ω , which is defined by $\omega = \frac{1}{2} \sum_1 c_1 z_1^2$, the concentrations c_1 are expressed in mol/unit volume. Table 1 gives a few typical values for $1/\kappa$ and ω for aqueous solutions of 25°C.

TABLE 1
Debye-length at 25°C and ionic strength for a number of electrolyte solutions

| 1-1 electrolyte | | $1/\kappa$ | ω | 2-2 electrolyte | | $1/\kappa$ | ω |
|-----------------|----------|----------------------|----------------------|-----------------|----------|-----------------------|----------------------|
| c | in mol/l | m | mol/l | c | in mol/l | m | mol/l |
| 10^{-5} | | 1.0×10^{-7} | 1.0×10^{-5} | 10^{-5} | | 5.0×10^{-8} | 4.0×10^{-5} |
| 10^{-3} | | 1.0×10^{-8} | 1.0×10^{-3} | 10^{-3} | | 5.0×10^{-9} | 4.0×10^{-3} |
| 10^{-1} | | 1.0×10^{-9} | 1.0×10^{-1} | 10^{-1} | | 5.0×10^{-10} | 4.0×10^{-1} |

In non-polar or slightly polar organic solvents the solubility and the degree of dissociation of electrolytes is usually much lower than in water. ϵ_r is also lower for these solutions, but this does not compensate for the reduced solubility. Consequently for electrolyte solutions in such organic solvents one generally has to reckon with relatively thick double layers.

2.1 Poisson-Boltzmann equation for flat plates

If one deals with flat plates and if the potential does not vary in directions parallel to the plate the Poisson-Boltzmann (from hereon abbreviated as P.B.) equation takes the form

$$d^2\psi/dx^2 = (2ze\alpha/c_0\epsilon_r) \sinh(ze\psi/kT) \quad (I-9)$$

where x is the coordinate perpendicular to the plate.

2.1.1 Potential-distance relation.

Obviously (I-9) has to be integrated twice in order to express ψ in terms of x , which has its origin on the particle surface. The first integration is performed using the boundary conditions $\psi = 0$ and $d\psi/dx = 0$ at $x = \infty$. The result is

$$d\psi/dx = -\sqrt{8nkT/\epsilon_r} \sinh(ze\psi/2\nu T) \quad (I-10)$$

In the second integration the boundary condition $\psi = \psi_0$ at $x = 0$ is introduced. ψ_0 is called the surface potential. The result can be given as

$$\tanh(ze\psi/4kT) = \tanh(ze\psi_0/4kT) \exp(-\kappa x) \quad (I-11)$$

Thus (I-11) is the general solution of the P.B. equation for flat plates. For small potentials, that is in case $ze\psi_0/4kT \ll 1$, the approximation $\tanh x \sim x$ can be used and then (I-11) reduces to

$$\psi = \psi_0 \exp(-\kappa x) \quad (I-12)$$

This equation shows that $\psi = \psi_0 \exp(-x/l)$, when $x = 1/\kappa$, illustrating why $1/\kappa$ is often called the thickness of the double layer. It is also easily proved that in this approximation the center of gravity of the double layer is exactly at a distance $1/\kappa$ from the surface. An increase in κ makes the double layer thinner ("compresses the double layer") and causes the potential to change more rapidly with the distance not only in the approximation (I-12) but also for the complete eq. (I-11).

In the derivation of (I-11) it has been assumed that the double layer is fully

developed, i.e. that the double layers of individual particles do not interfere. However, in relatively concentrated dispersions interference can occur, a phenomenon that is known as double layer overlap. This situation, which is particularly relevant for colliding colloidal particles, requires integration of (I-9) with adapted boundary conditions. It has extensively been dealt with by Verwey and Overbeek⁴, to which monograph we refer for further details.

2.1.2 Surface charge density and capacitance. The result obtained in the preceding section also enables us to derive a relation between the surface charge density σ_o and the surface potential ψ_o . Because σ_o is compensated by the space charge in the solution

$$\sigma_o = - \int_0^{\infty} \rho dx \quad (I-13)$$

Substitution of (I-5) into (I-13), taking into account that potential and charge variations along the y - and z -coordinates are assumed to be absent, leads to

$$\sigma_o = \epsilon_o \epsilon_r \int_0^{\infty} d^2\psi/dx^2 dx = - \epsilon_o \epsilon_r (d\psi/dx)_{x=0} \quad (I-14)$$

and insertion of (I-10) into (I-14) results in

$$\sigma_o = \sqrt{8n\epsilon_o \epsilon_r k^r} \sinh(z e \psi_o / 2kT) \quad (I-15)$$

For small values of ψ_o (I-15) simplifies to

$$\sigma_o = \epsilon_o \epsilon_r \kappa \psi_o \quad (I-16)$$

This actually is the equation for the capacitance per unit area (σ_o/ψ_o) of a plane condenser with plate distance $1/\kappa$. So again a physical meaning of $1/\kappa$ emerges.

Differentiation of (I-15) with respect to ψ_o provides the general equation for the (differential) capacitance of the diffuse double layer

$$\begin{aligned} C_d = d\sigma_o/d\psi_o &= \sqrt{2n\epsilon_o \epsilon_r z^2 e^2 / kT} \cosh(z e \psi_o / 2kT) \\ &= \kappa \epsilon_o \epsilon_r \cosh(z e \psi_o / 2kT) \end{aligned} \quad (I-17)$$

Equations (I-16) and (I-17) demonstrate that for a constant surface potential the capacitance, and thus the surface charge increases with increasing κ or with increasing electrolyte concentration.

2.2 Poisson-Boltzmann equation for spheres

For spherical symmetry the P.B. equation takes the form

$$(1/r^2) \frac{d}{dr} (r^2 \frac{d\psi}{dr}) = (2zen/\epsilon_o \epsilon_r) \sinh(z e \psi / kT) \quad (I-18)$$

In contrast with the situation for flat plates this equation cannot be solved analytically, except when the linearization for low potentials is applied. In that case the result is

$$\psi = \psi_a (a/r) \exp [-\kappa(r-a)] \quad (I-19)$$

where ψ_a is the surface potential of a spherical particle with radius a , and r is the distance to its center. From a comparison of (I-12) and (I-19) it can be concluded that for high values of κa double layers around spherical particles can be treated as if they have flat geometry.

From (I-19) it can rather easily be derived that for low surface potentials the total surface charge Q of a spherical particle amounts to

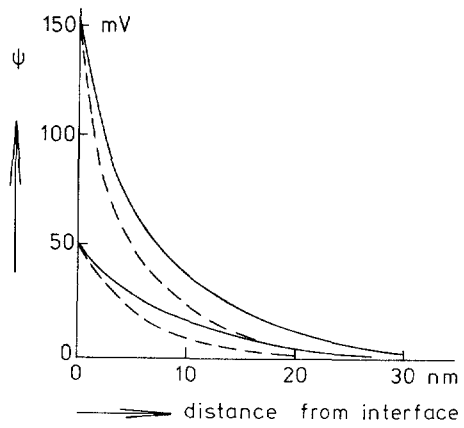
$$Q = 4\pi \epsilon_o \epsilon_r a (1 + \kappa a) \psi_a \quad (I-20)$$

Because $Q = 4\pi a^2 \sigma_o$ it is obvious that for $\kappa a \gg 1$, eq. (I-20) also reduces to the corresponding equation, (I-16), for flat plates.

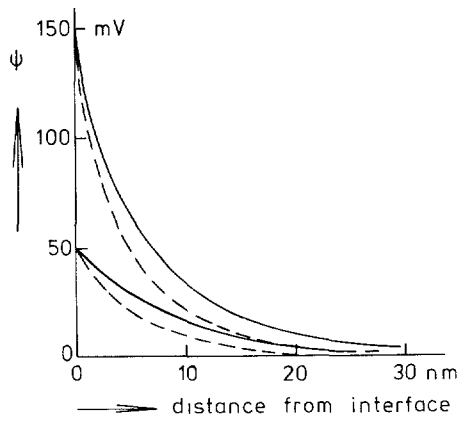
When the potentials are too high to allow linearization, numerical solutions of (I-18) have to take the place of analytical ones. Extensive numerical data, for a wide range of κa -values and also including asymmetrical electrolytes, have been tabulated by Loeb et al.⁵ Space does not allow to cover them extensively in this text. However, in fig. 2 some results for spheres are compared with those for flat plates. These graphs visualize that for spherical symmetry the potential falls off more rapidly than for flat plates, and that is more pronounced the smaller the radius of the particle. It is also seen that for spheres as well as for flat plates, bivalent ions are much more effective in compressing the double layer.

Stigter⁶ formulated interpolation equations for the tables of Loeb et al., whereas White⁷ recently published approximate analytical solutions. For finite concentrations of the dispersed particles, again the possibility of double layer overlap has to be taken into account. This has recently been done in numerical calculations of Mille and Vanderkooi⁸.

Examples of practical systems with spherical dispersed particles are emulsions, (monodisperse) lattices, small surfactant micelles and some proteins.



a



b

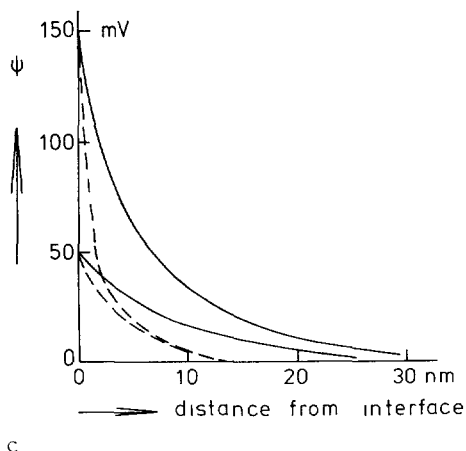


Fig. 2. Potential ψ as a function of the distance from the particle surface. Upper curves refer to $\psi_0 = 154$ mV, lower curves to $\psi_0 = 51$ mV
 a) 10^{-3} M 1-1 electrolyte; drawn lines: flat plates; dashed lines: spheres with a radius of 10 nm.
 b) 10^{-3} M 1-1 electrolyte; drawn lines: spheres with a radius of 100 nm; dashed lines: spheres with a radius of 10 nm.
 c) spheres with a radius of 100 nm in 10^{-3} M 1-1 electrolyte (drawn curves) and in 10^{-3} M 2-2 electrolyte (dashed curves).

2.3 Poisson-Boltzmann equation for cylinders

Polyelectrolytes are long chain polymer molecules containing a large number of ionizable groups along the chain. Although in electrophoresis some polyelectrolytes can occasionally be considered as impermeable or partially permeable spheres, most polyelectrolytes, being linear molecules, can better be treated as (kinked) cylindrical rods. Thus, for these cases it is essential that the P.B. equation is solved for cylindrical geometry. The Laplace operator then reads $\nabla^2 = (1/r) \times d[r(d\psi/dr)]/dr$. Just like in case of spherical particles the ensuing equation cannot be solved analytically, so that one has to recur again to numerical procedures or to approximate solutions. The first approximation was introduced by Dube⁹ and Gorin¹⁰. However, it suffers from the drawback that it is only valid for small potentials. Of much wider applicability is the approximation introduced by Philip and Wooding¹¹. These authors proceed by dividing the double layer into two parts, the boundary between them being characterized by the value of κr that makes $ze\psi/\kappa T$

equal to one. For the inner region it is assumed that all co-ions are absent, so that the corresponding exponential term in the r.h.s. of the P.B. equation can be neglected. In passing, it can be mentioned that exclusion of co-ions from regions close to the central particle is quite a general phenomenon for any type of double layer, it is known as negative adsorption. As to the outer region the complete linearized equation is used. The system of equations thus arising can be solved analytically. Both Philip and Wooding¹¹ and v.d. Drift¹² have compared the results of this approximation with exact numerical solutions and arrived at the important conclusion that the available analytical solutions, although not being exact, have such a degree of accuracy that they can safely be used for subsequent purposes, e.g. in a theory of electrophoresis.

A discussion on polyelectrolytes as charged linear particles must also include the concepts of Manning¹³. Manning considers the particles as rods without a volume, thus reducing the charge to a line charge. It then appears that the linear charge density cannot exceed a certain value and any dissociation above that limit is offset by a "condensation" of counterions onto the line charge. The extent of this condensation is dependent on the charge number of the counterions and on the ionic strength¹⁴. The remaining cylindrical double layer may then be treated using the linearized Debye-Hückel theory.

Manning's theory aims in particular at the explanation of thermodynamic properties of polyelectrolytes and of the mobility of the counterions. So far it has not been used to estimate the electrophoretic mobility of the polyanion.

2.4 Modifications of the Poisson-Boltzmann equation

In the preceding derivation and integrations of the P.B. equation a substantial number of assumptions has been made, e.g. that the ions are point charges and that the dielectric constant is independent of the concentration and the (often high) electrical field strength. These assumptions have been the subject of many critical objections, a review of which has been given by Bell and Levine¹⁵. From extensive theoretical studies these authors^{15,16} conclude that many of the effects are mutually compensating and that for flat plates the corrections to the P.B. equation are not excessive for 1-1 electrolyte concentrations below 0.1 M and surface potentials not exceeding 75 mV. Another aspect deserving attention is the assumed homogeneous distribution of the surface charges. However, despite the actually discrete character of these charges and their often relatively large mutual separations, it can be shown by statistical mechanical arguments that the potential distribution in the double layer may be described by a continuum theory¹⁷.

I.3 STERN-CORRECTION

Contrary to the assumption in diffuse double layer theory, ions do have a finite size and treating them as point charges is a simplification. This finite size shows up in the first place in preventing the center of the ions, so the center of the charge, to approach the interface to distances smaller than the ion radius. Therefore, in an actual situation a charge-free region is present between the surface charge and the diffuse charge in the solution. Taking this aspect into account eliminates the impossible consequence, implicit in simple diffuse double layer theory, that concentrations at the surface can grow as high as 200 M. This improvement was first introduced by Stern¹⁸, who also pointed out that counterions not only interact with the surface by electrical forces, but frequently by chemical forces too, in which case specific adsorption is said to occur. The surface charge is then compensated by the sum of the charges in the diffuse and in the Stern-layer:

$$\sigma_o = -(\sigma_s + \sigma_d) \quad (\text{I-21})$$

Following Stern, one usually describes σ_s by a Langmuir isotherm. In its simplest form, when only specific adsorption of counterions is considered, it reads in the case of a negatively charged surface

$$\sigma_s = \frac{ze\Gamma_o}{1 + (1/Kc) \exp(ze\psi_d + \phi)/kT} \quad (\text{I-22})$$

Γ_o is the total number of available adsorption sites per unit area, K a proportionality constant and c the bulk concentration of the ions. ϕ is called the specific adsorption potential, although it is an energy-, rather than a potential term. ϕ may discriminate between ions of identical charge number, thus explaining such specific effects as the lyotropic order. Moreover, ϕ may be a function of the surface charge.

Stern's approach has since been refined, particularly by D.C. Grahame, who introduced the conceptions Inner and Outer Helmholtz Plane. The specifically adsorbed ions are in the I.H.P., the diffuse layer ends at the O.H.P. and these two planes are in general not identical. For a detailed treatment of these notions and of refined electrical double layer theories in general we refer to the monograph by Sparnaay¹⁹.

Of course the presence of the Stern layer (frequently also called molecular condenser) has important consequences for the potential distribution in the solution. In fig. 3 the distribution has been sketched that goes along with the presence of merely a charge-free layer. It can be seen that across the molecular condenser the potential decays linearly from ψ_o to the value ψ_d at the boundary between Stern and Gouy layer. This implies that actually in all diffuse double layer equations ψ_o has to be replaced by ψ_d . Farther away from the surface than

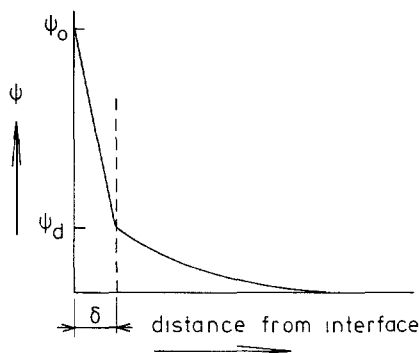


Fig. 3 Potential as a function of distance in the presence of a charge-free Stern layer of thickness δ and a diffuse layer for $x > \delta$.

ψ_d the character of the Gouy layer is not altered e.g. with regard to the compressing effect of κ .

The overall value of the capacitance of the double layer, C , in the presence of a molecular condenser results from the combination of the capacitances of Stern and Gouy layer placed in series:

$$(1/C) = (1/C_s) + (1/C_d) \quad (\text{I-23})$$

It can be inferred from (I-23) that C is dominated by the smallest of its two contributions. Because C_d is an increasing function of the concentration and of ψ_d (cf. eq. (I-17)), C will mainly reflect C_d at low values of ψ_d and σ , and C_s at higher values of these parameters. In the latter case any dependence of C_s on σ_0 will also become manifest.

I.4 EXPERIMENTAL VERIFICATION OF DOUBLE LAYER THEORIES

Double layer theories have been the subject of numerous investigations. The system most extensively studied in this respect has been the interface between mercury and aqueous electrolyte solutions. Experimentally either electrocapillary

curves or differential capacitances were measured. In some studies both approaches were used and the results could be compared. For a review of all the conclusions to be drawn from these data we refer to Sparnaay¹⁹ again. Suffice it to say that in general the Stern-Gouy-Chapman picture has been confirmed.

In the mercury-aqueous electrolyte system the surface charge and the surface potential are modified by applying an external voltage. In most colloidal systems, however, the surface charge is obtained by adsorption of ions or - in particular with proteins and other polyelectrolytes - by dissociation of surface groups. In favorable cases the charge may be determined by chemical analysis e.g. by titration techniques. Various oxides and the silver halides have been used for such studies on the double layer. Among the latter silver iodide is most outstanding, because it combines a relatively wide range of accessible potentials with the possibility to relate direct double layer data to data on colloidal stability and electrokinetics. In a recent review²⁰ it has been outlined that for silver iodide the basic ideas of current double layer theory are also applicable. At the same time it is observed that quantitative differences with mercury exist, that emphasize the importance of the specific nature of the Stern layer. In fig. 4 some data representative for silver iodide are reproduced. They illustrate, e.g., that at

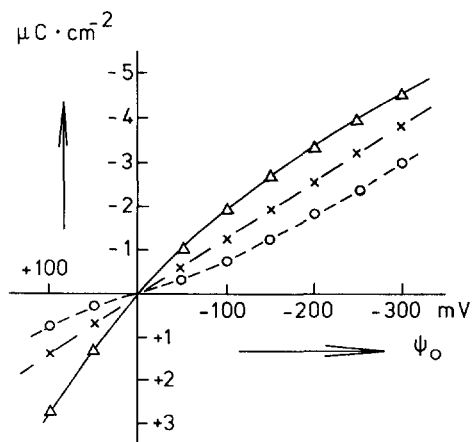


Fig. 4. Surface charge σ_0 as a function of surface potential ψ_0 for silver iodide in aqueous KNO_3 solutions.

Δ — Δ 0.1 M \times — \times 0.01 M \circ — \circ 0.001 M

low ionic strength (10^{-3} M) and in the neighborhood of the point of zero charge σ_0 progressively increases with ψ_0 , in accordance with diffuse double layer theory (e.g. eq. (I-15)). At high ionic strength (10^{-1} M) the differential capacitance, being the slope of the curves, is usually much higher than at low ionic strength. Because C is now dominated by the Stern layer its variation reflects the dependence of C_s on σ_0 as was anticipated in the discussion of section I 3.

In practical systems compression of the double layer results in an increase of the charge and/or a decrease of the potential. The precise conditions (e.g. the amount of potential determining electrolyte and the total surface area) dictate whether the surface charge or the surface potential remains constant, or that both quantities are adapted, upon changing the ionic strength of the solution.

I 5 THE POSITION OF THE SLIPPING PLANE IN ELECTROKINETICS

All electrokinetic phenomena deal with the tangential movement of particle and surrounding liquid. In discussing these processes it is important to know the exact position of the slipping plane relative to the two phases. Unfortunately, no unambiguous statements can be made as to this position because a complete theory on the slipping process is not available. However, from a vast amount of experimental data it may be concluded that the slipping plane does not coincide with the particle surface, but is situated at some distance in the solution. Apparently a stagnant layer prevents displacement of the liquid close to the surface. However, this qualitative notion still leaves us with the question about the *exact* position of the slipping plane and thus about the value of the potential (the ζ -potential) at this position. Considering double layer-, stability- and electrokinetic data on silver iodide, Lyklema²¹ recently concluded that, although exact answers still cannot be given, it remains a reasonable assumption to set ζ equal to ψ_d .

The supposed equality of ζ and ψ_d of course implies that ζ is equally sensitive to changes in surface charge, surface potential and ionic strength as ψ_d is. So, here we have the justification for the ample attention given to diffuse double layer theory in the preceding sections. The relation between ζ and electrophoretic mobility will be discussed in the following sections.

II. THE THEORY OF ELECTROPHORESIS

II.1 INTRODUCTION

The most simple theoretical approach to electrophoresis would lead us to expect that the electrophoretic velocity, v , is equal to the force on the particle (charge, Q , times field strength, E) divided by the friction constant, f ($f = 6\pi\eta a$ for a sphere of radius a in a medium with viscosity η) Or, introducing the mobility, u , we would have

$$u = \frac{v}{E} = \frac{Q}{f} \quad (\text{II-1})$$

This approach, however, neglects the fact that the countercharge, $-Q$, is often quite close to the particle surface and is subjected to a force, $-Q \times E$. By hydrodynamic interaction a substantial fraction of this counterforce is transmitted to the particle, thus reducing its electrophoretic mobility, often by one or more orders of magnitude. This *hydrodynamic* effect is called *electrophoretic retardation*. Moreover, since particle and countercharge move in opposite directions, and a certain time, the relaxation time τ , is required to replace the counterions that have moved away by new ones, the double layer is distorted. This distortion creates a field opposite to the applied field, E , and this *relaxation field* slows down the particle by *electric interaction*. The *relaxation effect* is usually not as large as the electrophoretic retardation, but a reduction of the mobility by 10-50% is not exceptional.

The main difficulty in the theory of electrophoresis is the correct calculation of these two retarding effects.

Theoretically, the electrophoretic mobility is expected to be independent of the field strength, as long as the latter remains below 10000 V cm^{-1} , and this is confirmed empirically. We shall limit our discussion to low field strengths.

II.2 ELECTROPHORESIS OF SPHERICAL PARTICLES

We shall deal with the electrophoresis of spheres fairly extensively, not because most particles are spherical (although emulsions, lattices, micelles and some proteins offer good examples), but because this case has been studied so thoroughly. To begin with, we omit the relaxation effect (i.e. we treat the double layer as undistorted), but it will be included later in this section.

2.1 Method of Huckel and Onsager

Closely connected with his work with Debye²² on the conductivity of strong electrolytes, Huckel²³ published a paper on the electrophoresis of the sphere. In this paper he solved the Navier-Stokes equations for the stationary motion of a sphere surrounded by an electrical double layer in an applied field, E , and found for the mobility, u ,

$$u = \frac{2\epsilon_0 \epsilon_r \gamma}{3\eta} \quad (\text{II-2a})$$

or rather, since he used non-rationalized three quantity equations, without a separate electrical dimension,

$$u = \frac{\epsilon_r \zeta}{6\pi\eta} \quad (\text{II-2b})$$

In these equations ζ is the surface potential (more precisely, the potential at the slipping plane) and η is the viscosity of the liquid.

A few years later, Onsager²⁴ presented a simple and illuminating derivation of eq.(II-2) that we shall repeat here. The ionic atmosphere around the particle can be divided in concentric spherical shells of radius, r , and thickness, dr , as shown in figure 5. The field, E , exerts a force $4\pi r^2 \rho E dr$ on the shell and this results in the shell moving with a velocity, v , with respect to its surroundings, but drawing

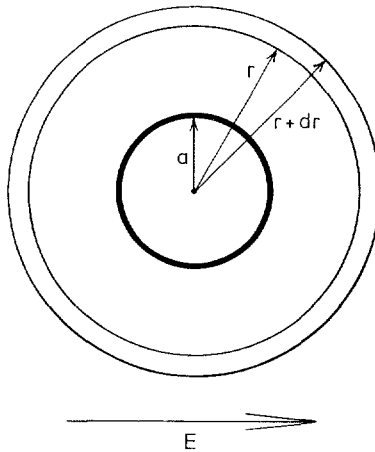


Fig. 5. Particle with radius a , surrounded by an ionic atmosphere, consisting of spherical shells, one of which is shown, in an electric field, E .

everything (liquid and particle) within it along. v is found by the application of Stokes' law.

$$v = \frac{4\pi r^2 \rho E dr}{6\pi \eta r} \quad (\text{II-3})$$

The total ionic atmosphere gives its innermost layer and thus the particle a velocity

$$v_{\text{atm}} = \int_a^{\infty} \frac{4\pi r^2 \rho E dr}{6\pi \eta r} \quad (\text{II-4})$$

The field, acting on the particle charge, Q , gives the particle a velocity v_{part} with respect to its immediate surroundings

$$v_{\text{part}} = \frac{QE}{6\pi \eta a} \quad (\text{II-5})$$

The net velocity of the particle with respect to the liquid at infinity, v , is the sum of (II-4) and (II-5), which counteract one another, since ρ and Q have opposite signs. The atmosphere decreases the velocity of the particle.

$$v = \frac{QE}{6\pi \eta a} + \int_a^{\infty} \frac{4\pi r^2 \rho E dr}{6\pi \eta r} \quad (\text{II-6})$$

This expression is easily transformed into (II-2) by using

$$Q = - \int_a^{\infty} 4\pi r^2 \rho dr \quad (\text{II-7})$$

which expresses the electroneutrality of particle plus atmosphere and by applying Poisson's law for spherical symmetry:

$$\rho = -\epsilon_r \epsilon_o \nabla^2 \psi = - \frac{\epsilon_r \epsilon_o}{r^2} \frac{\partial^2}{\partial r^2} (r\psi) = - \frac{\epsilon_r \epsilon_o}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial \psi}{\partial r}) \quad (\text{II-8})$$

The transformation runs as follows:

$$\begin{aligned} v &= + \frac{2\epsilon_r \epsilon_o E}{3\eta a} \int_a^{\infty} \frac{\partial}{\partial r} (r^2 \frac{\partial \psi}{\partial r}) dr - \frac{2\epsilon_r \epsilon_o E}{3\eta} \int_a^{\infty} \frac{\partial^2}{\partial r^2} (r\psi) dr = \\ &= \frac{2\epsilon_r \epsilon_o E}{3\eta} \left[- \frac{1}{a} \alpha^2 \left(\frac{\partial \psi}{\partial r} \right)_a + \left(\frac{\partial}{\partial r} (r\psi) \right)_o \right] = + \frac{2\epsilon_r \epsilon_o \zeta E}{3\eta} \end{aligned} \quad (\text{II-9})$$

which proves eq.(II-2a).

Remarkably enough, neither the size of the particle nor the thickness of the double layer shows explicitly, if the mobility is expressed as a function of the surface potential, ζ .

2.2 Smoluchowski's equation

Already in 1903 and especially in 1914, von Smoluchowski²⁵ derived an equation very similar to Hückel's eq.(II-2b), but differing from it by having 4π instead of 6π in the denominator.

$$u \text{ (Smol.)} = \frac{\epsilon_r \zeta}{4\pi\eta} = \frac{\epsilon_o \epsilon_r \zeta}{\eta} \quad (\text{II-10})$$

In his very elegant derivation, which applies to particles of arbitrary shape, Smoluchowski assumes that the double layer is thin compared to any dimension of the particles and that the applied field is distorted so as to run parallel to the particle-liquid interface at that interface and close to it (see fig.6).

As a consequence of the distortion of the field, the atmosphere is on the average in a field smaller than E and thus it retards the particle less than in Hückel's and Onsager's calculation.

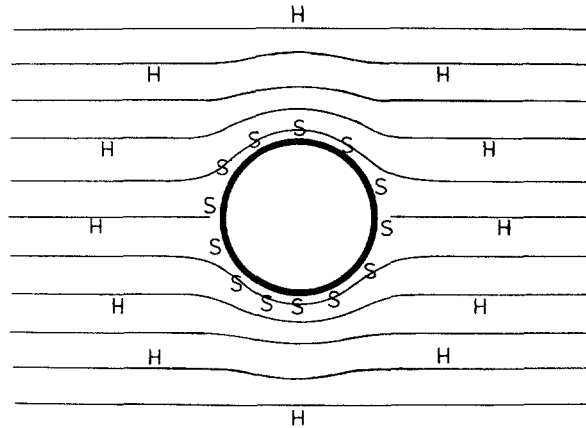


Fig. 6. Illustrating that a thin double layer (S for Smoluchowski, $1/\kappa \ll a$) is in the distortion region, whereas a thick double layer (H for Hückel, $1/\kappa \gg a$) is mostly in the undisturbed field.

Eq.(II-10) with the sign reversed is also valid for electro-osmosis, as Smoluchowski demonstrated as follows. An electric field, E , is applied parallel to the interface between a solid and a liquid. The solid carries a surface charge compensated by a diffuse double layer in the liquid. We consider a thin layer of liquid of area, A , and thickness, dx , parallel to the surface at a distance, x . The electric field E exerts a force, $A\rho E dx$, on this layer. The viscous friction tends to retard the layer with a force, $-A\eta dv/dx$ at the plane x , whereas it tends to accelerate it with a force $+A\eta(dv/dx)_{x+dx}$ at the plane $x+dx$, where v is the velocity of the liquid parallel to the interface. In the stationary situation, the net force on the layer is zero, or

$$A\rho E dx - A\eta(dv/dx)_x + A\eta(dv/dx)_{x+dx} = 0 \quad (\text{II-11})$$

$$\text{or: } A(\rho E dx + \eta \frac{d^2v}{dx^2} dx) = 0 \quad (\text{II-12})$$

With $\rho = -\epsilon_r \epsilon_0 d^2\psi/dx^2$ we find:

$$\epsilon_r \epsilon_0 E d^2\psi/dx^2 = \eta d^2v/dx^2 \quad (\text{II-13})$$

A first integration with $d\psi/dx = dv/dx = 0$ for $x \rightarrow \infty$ leads to

$$\epsilon_r \epsilon_0 E d\psi/dx = \eta dv/dx \quad (\text{II-14})$$

The second integration with $\psi = \zeta$ and $v = 0$ for $x = 0$ and $\psi = 0$ and $v = v$ (electro-osmosis) for $x \rightarrow \infty$ gives

$$\frac{v(\text{electro-osmosis})}{E} = -\frac{\epsilon_r \epsilon_0 \zeta}{\eta} \quad (\text{II-15})$$

2.3 Henry's contribution

A few years after the appearance of Hückel's paper²³, Henry²⁶ showed conclusively that the Smoluchowski approach is correct for thin double layers ($\kappa a \gg 1$), and the Hückel-Onsager equation is correct for thick double layers ($\kappa a \ll 1$). Henry bridged the gap and gave equations for intermediate values of κa both for spheres and for cylinders, using the linearized Debye-Hückel approximation (eqs.I-7,I-19) for the structure of the double layer. For that reason, and because he neglected the relaxation effect, his results are only valid for small values of ζ . Figure 6 illustrates the different influences of the field distortion for thin and for thick double layers, and figure 7 gives a graphic representation of Henry's results.

Table II gives a few numerical values of $3\eta\eta/2\epsilon_r \epsilon_0 \zeta$ for the non-conducting sphere.

TABLE II

 $f(\kappa a) = 3u(\text{sphere}) \eta / 2\epsilon_r \epsilon_0 \zeta$ as a function of κa

| κa | 0.1 | 0.3 | 1 | 3 | 5 | 10 | 20 | 50 | 100 | 1000 |
|---------------|----------|---------|--------|--------|-------|------|------|-------|-------|-------|
| $f(\kappa a)$ | 1.000545 | 1.00398 | 1.0267 | 1.1005 | 1.163 | 1.25 | 1.34 | 1.424 | 1.458 | 1.495 |

The cases

- no field distortion or conductivity of sphere and medium are equal, and
- the perfectly conducting sphere

have hardly any real practical significance, since the smallest amount of polarization is sufficient to prevent the current to cross the particle medium interface.

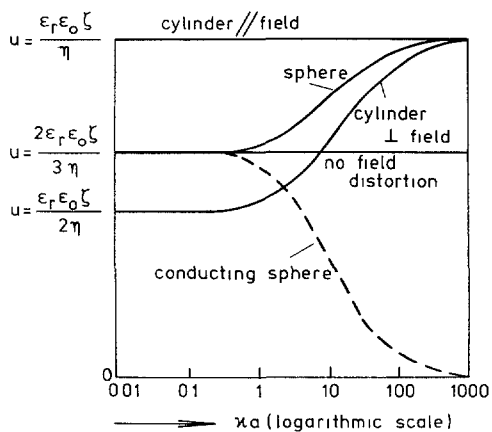


Fig. 7. Electrophoretic mobility for spheres and cylinders as a function of $\log(\kappa a)$. Debye-Hückel linearization (eq. I-7) used.

2.4 The relaxation effect

So far, we have neglected the distortion of the ionic atmosphere, which leads to the relaxation effect. Figure 8 illustrates how an originally symmetric atmosphere, which is forced to move with respect to the particle, is dispersed at one side and rebuilt at the other, but with a time lag, which causes the atmosphere to become asymmetric, creating a field, ΔE , opposed in direction to the applied field E and slowing down the particle.

The actual calculation of the relaxation field is difficult. It already formed one of the more difficult aspects in the Debye-Hückel theory, where it was possible to consider the ions as point charges.

The great difference in size between the particle and the atmospheric ions and the necessity to go beyond the linear approximation of the P.B. equation make the problem all the more difficult. In the nineteen forties, Booth²⁷ and Overbeek²⁸ formulated solutions in the form of expansions in a power series of increasing powers of $ze\tau/kT$, which showed that the relaxation effect is particularly important in the region $1 < \kappa a < 10$ and that it vanishes at low and at high values of κa . Later, Wiersema et al.²⁹ applied a computerized numerical procedure to solve eight simultaneous differential equations (three components of the liquid velocity, pressure in the liquid, concentrations of cations and anions and local potential

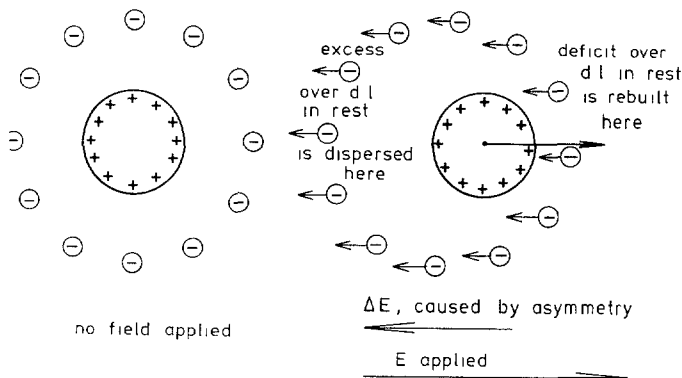


Fig. 8. Illustrating schematically the formation of the relaxation field, ΔE .

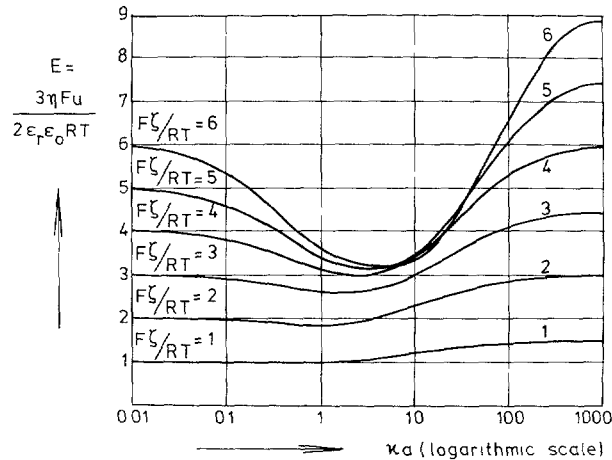


Fig. 9. Dimensionless electrophoretic mobility, \bar{E} , as a function of κa for a series of values of the ζ -potential. The electrophoretic mobility $\bar{E} = \frac{2\epsilon_r \epsilon_0 RT}{3\eta u} E$. The curves are given for $\zeta/(RT/F) = \zeta/(k''/e) = 1, 2, 3, 4, 5$ and 6 .

inside and outside the sphere, using the complete P.B. equation (I-6) in successive approximations. They confirmed the results of Booth and Overbeek for low values of ζ and extended the calculations to $z\zeta \sim 150$ mV. Figure 9 gives their results for particles embedded in 1-1 electrolytes of conductivity equal to that of KCl. The influence of the ionic mobility proved to be of only secondary importance. For other charge numbers of the electrolyte and for other ionic mobilities, the reader is referred to the original paper²⁹ or to a more condensed version³⁰. It is obvious from figure 9 that at high and at low κa the mobility and ζ -potential are nearly proportional and that this is also true at intermediate values of κa for low mobilities and low ζ (say $\zeta < 1.5 \frac{k''}{e} \sim 40$ mV). But for high ζ -potentials and intermediate values of κa (say $2 < \kappa a < 50$) the mobilities become nearly independent of ζ . In that region electrophoresis is not a good method to obtain information on surface charge or surface potential.

In most practical situations, it is essential to take both electrophoretic retardation and relaxation effect into account, although it is often possible to use analytical approximations instead of the computer values of figure 9, see²⁹.

2.5 Stern layer and slipping plane

It should be emphasized that all models treated above describe the particle as a rigid sphere, with a double layer containing point ions which may approach the surface infinitely closely. A more realistic model with finite size ions leaving a "Stern layer" of thickness, δ , free of charge, is still covered by the calculations, if it is assumed that the slipping plane (surface of shear) coincides with the O.H.P. at a distance δ from the surface and that the layer between the O.H.P. and the surface does not contain any mobile ions. In that case, ζ -potential and Stern-potential are identical. For locations of the slipping plane further outside than the O.H.P., electrophoresis leads to a ζ -potential which is lower than ψ_δ , but if the slipping plane is closer to the surface than the O.H.P., the ζ -potential cannot be found from Wiersema's theory since it does not take a charge free layer that is still mobile into account.

II.3 ELECTROPHORESIS OF CYLINDRICAL PARTICLES

When considering the electrophoresis of cylindrical particles, two facts should be kept in mind. In the first place, orientation is important, and secondly, most considerations about cylinders neglect end-effects, the results being obtained by considering infinitely long cylinders. The cylinder may be an acceptable model for rod-like particles such as tobacco mosaic virus, and for stiff or flexible long chain polyelectrolytes for which DNA and polyacrylic or polymethacrylic acid are examples.

3.1 Neglecting the relaxation effect

Henry²⁶, again neglecting the relaxation effect, solved the hydrodynamic equations for two orientations of the cylinder, viz. parallel or perpendicular to the applied field. His results are given in figure 7 for cylinders of radius a . For a cylinder parallel to the field, the field strength has the value E and is parallel to the surface everywhere in the solution. Therefore, Smoluchowski's equation (II-10) applies, irrespective of the value of κa . The field around a cylinder in perpendicular orientation is distorted in a similar way as sketched in figure 6, and this results in an electrophoretic mobility that depends on κa , with the Smoluchowski value (II-10) at high κa and only half that value at low κa .

$$u(\text{cyl.} \perp E)_{\kappa a \rightarrow 0} = \frac{\epsilon_r \zeta}{8\pi\eta} = \frac{\epsilon_0 \epsilon_r \zeta}{2\eta} \quad (\text{II-16})$$

It should further be realized, that at the extreme values of κa eqs. (II-2), (II-10) and (II-16) are valid, even if ζ is large ($|e\zeta/kT| > 1$) and that this is also true for the cylinder parallel to the field at any κa . But the transition for intermediate values of κa , as given in fig. 7, has been found by Henry using the linear Debye-Hückel approximation and is, therefore, not strictly valid for high ζ . However, the necessary corrections are smaller than those for the relaxation effect.

3.2 Averaging over different orientations

For a cylinder oriented at an arbitrary angle, θ , between its axis and the field, the field may be split into two components, one, $E \cos \theta$, parallel to the cylinder axis and one, $E \sin \theta$, perpendicular to it. Each of these components results in a velocity of the cylinder, one parallel and the other perpendicular to the axis. Vectorial addition of these two velocity components gives the net velocity of the cylinder and when this velocity is averaged over a random distribution of orientations, a simple result is obtained, viz.,

$$u \text{ (average over all orientations)} = \frac{1}{3} u_{//} + \frac{2}{3} u_{\perp} \quad (\text{II-17})$$

where $u_{//}$ and u_{\perp} are the mobilities for parallel and perpendicular orientation resp. De Keizer, Van der Drift and Overbeek³¹ have shown this relation to be valid in the absence of relaxation. Stigter³² has extended the proof so as to include the relaxation effect.

At low field strengths, as long as Ohm's law is obeyed, the field does not orient the cylinder against the randomizing effect of Brownian motion. Similarly, a flexible polyelectrolyte coil may be considered as a collection of cylindrical pieces with on the average random orientation.

3.3 Relaxation effect for cylinders

Stigter³², using an approach very similar to that of Wiersema et al.²⁹, computed the mobility of the cylinder perpendicular to the field, including the relaxation effect. He further concluded that for parallel orientation the relaxation effect may be neglected, and then using eq (II-17) applied his results to polyelectrolytes such as DNA, PAA and PMA. In the middle range of κa he obtained relaxation effects as high as 20%.

Shortly before, Van der Drift¹² had used Philips' and Wooding's¹¹ description of the cylindrical double layer at high potentials ($e\zeta/kT > 1$) to improve Henry's mobility values, but he applied a semi-empirical method (Moller et al.³³) based on the essential equality of the relaxation force on the particle and on the charge in its atmosphere, to correct for the relaxation effect. For half-ionized PMA, Van der Drift found relaxation corrections of 40-60%.

We conclude that until Stigter's results³² are completely published, the theoretical interpretation of the electrophoretic mobility of cylindrical particles must be limited to low ζ -potentials, using eq (II-17) for averaging over orientations, and using the numerical values obtained by Abramson, Gorin and Moyer³⁴ for Henry's equation²⁶ for the cylinder perpendicular to the field.

II 4 ELECTROPHORESIS OF THE POROUS SPHERE

The electrophoresis of polyelectrolytes has been interpreted in terms of the randomly oriented cylinder as was mentioned in the previous section. An older model is that of the porous sphere. The porous sphere, with the solvent flowing more or less freely through it, was quite a successful model for hydrodynamic properties (viscosity, diffusion, sedimentation) of solutions of uncharged polymers. The model has been extended to polyelectrolytes, the assumptions being made of a uniform or Gaussian distribution of the fixed charges, a similar distribution of the chain elements, each element having the same friction factor with respect to liquid flowing past it and a Debye-Hückel type interaction between the free, low molecular weight ions and the fixed charges.

If the relaxation effect and the deformation of the applied field by the difference in conductivity inside and outside the porous sphere are neglected, the further mathematical treatment is simple. Overbeek and Stigter³⁵ obtained the result that for small κR (R is the radius of the sphere) the countercharge has no influence on the mobility and the sphere moves with the friction factor of a partially drained coil (Debye and Bueche³⁶, Brinkman³⁷). For large κR , the sphere behaves as freely drained, its friction factor is the sum of the friction factors, \bar{f} , of the chain elements and the counterions move through the porous sphere with the same velocity that they would have in free solution. Figure 10 shows the transition between the two cases.

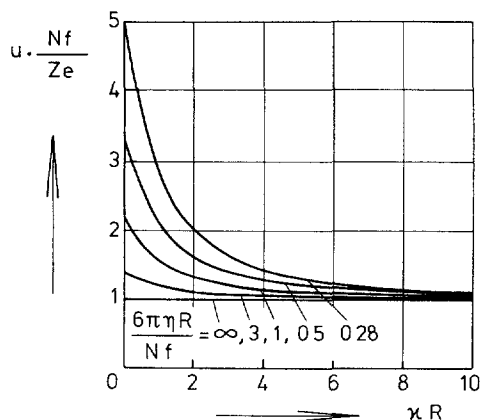


Fig 10 Electrophoretic mobility of a porous sphere with radius R , charge Ze , containing N elements, each with a friction constant, \bar{f}

Although the model is in qualitative agreement with experiments, close consideration¹² shows that it is only realistic for compact, highly crosslinked polymers. The usual polyelectrolyte coils are so open, that a uniform distribution of chain elements, fixed charges and countercharges is quite unrealistic. A much better model is that of a loosely coiled cylinder surrounded by a fairly compact double layer as shown schematically in figure 11.

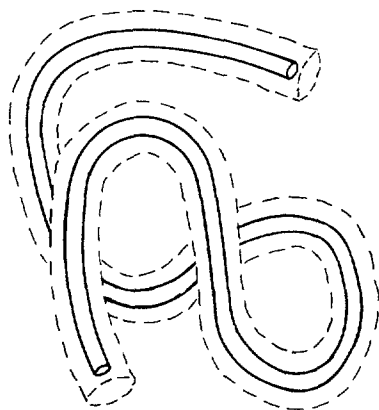


Fig. 11. Coiled cylinder surrounded by a double layer.

II.5 PARTICLES OF ARBITRARY SHAPE

After the discussion of the difficulties arising in the formulation of an electrophoresis theory for three rather simple models, one might wonder whether any useful interpretation can be given for particles of arbitrary shape. In fact, however, relatively simple interpretations are possible, at least for the limits of very high and very low values of κ (i. e. of the electrolyte concentration)

5.1 Small κ

If the largest linear dimension, b , of a particle is much smaller than $1/\kappa$, or in other words $\kappa b \ll 1$, ionic atmosphere effects, both electrophoretic and relaxation retardation, are bound to be minor, and the mobility is simply equal to the

charge, Ze , divided by the friction factor, f ,

$$u = \frac{Ze}{f} \quad (\text{II-18})$$

The same friction factor can be found from rates of diffusion or sedimentation, and since the charge may be determined by analysis, eq.(II-18) can be tested or be used for the calculation of one of its three elements from the two others. In aqueous media, however, it is difficult to decrease κ below $(100 \text{ nm})^{-1}$, and thus the case $\kappa b \ll 1$ only applies to small particles (say $< 10 \text{ nm}$ or even $< 1 \text{ nm}$). In non-polar media, where $1/\kappa$ may easily be several μm , eq.(II-18) is the obvious one for the interpretation of electrophoresis.

5.2 Large κ

In the context of irregularly shaped particles, large κ means $\kappa a \gg 1$, where a is the smallest local radius of curvature of the particle surface. In that case, the Smoluchowski equation (II-10) applies, even at large charge and ζ -potential. Overbeek³⁸ has shown that under these circumstances the relaxation effect becomes negligible (see also our figures 7 and 9). The electrophoretic retardation, however, is then quite large, slowing down the mobility as compared to eq.(II-18) in the ratio of about $1/\kappa b$. It is in particular under these conditions of large particle size and/or thin double layers, that the ζ -potential has such a unique position in the interpretation of electrophoresis.

II 6 ELECTROPHORESIS AS A FUNCTION OF THE CHARGE OF THE PARTICLES AND OF THE POTENTIAL DIFFERENCE BETWEEN THE PHASES

So far, we have interpreted the electrophoretic mobility nearly exclusively in terms of the ζ -potential, with some correction for relaxation. Unfortunately, there is no independent way to measure ζ , and no way either to determine the exact location of the slipping plane. So it should be asked whether an interpretation in terms of the surface charge, rather than the ζ -potential, might not have advantages. One obvious advantage is the fact that the particle charge is carried by ions, and thus can be determined in principle by chemical analysis. Moreover, the charge can be manipulated by addition of easily adsorbable ions, by a change in pH, or by chemical reaction. On the other hand, the charge as determined analytically, q_1 , and the electrokinetic charge, q_2 , need not be identical, and in general are not identical, the difference being formed by that part of the atmospheric charge that is situated between the surface and the slipping plane. Nevertheless, a comparison between q_1 and q_2 remains of interest, since it gives at least some information on the location of the slipping plane. At low ionic strength, the difference between q_1 and q_2 may be expected to be small, but at high ionic strength it may be large due to the compression of the double layer and the steep

decay of potential with distance at high ionic strength. Figure 12 illustrates this.

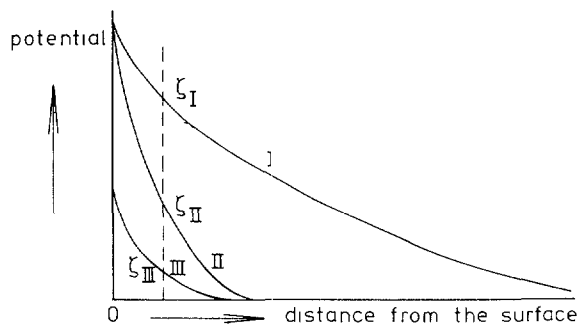


Fig. 12. Illustrating the influence of compression of the double layer on ζ . The dotted line represents the slipping plane.

I. Low ionic strength

II. High ionic strength. Surface potential, ψ_0 , as in I.

III. High ionic strength. Surface charge, q_1 , as in I.

The surface charge density is proportional to the slope of the potential — distance line at $x = 0$ (eq. I-14). It can be seen that $q_2(I) \sim q_1(I)$ but $q_2(II, III) < q_1(II, III)$

The ζ -potential may also be compared to the surface potential, ψ_0 , which in many cases is equal to the potential difference between the particle phase and the solution phase, as it contributes to the e.m.f. of a galvanic cell. Since the absolute value of such a potential difference is not accessible to measurement, the point of zero charge should be taken as the point where ψ_0 and ζ are both zero. Such a comparison, if made for a number of ionic strengths, may show whether the assumption that $\zeta \sim \psi_d$ (the Stern-potential) is justified (cf. Lyklema²¹)

Not enough work has been aimed in this direction, and what has been done has not always been too successfully interpreted. One conclusion might be that the slipping plane shifts away from the surface with decreasing ionic strength.

The electrophoretic mobility and the ζ -potential reflect changes in ψ_0 , q_1 , κ , and also in the detailed composition of the solution, since adsorption of ions or neutral substances may affect ζ .

On the whole, changes in the surface potential ψ_0 are reflected somewhat more weakly (say as a fraction between 0.5 and 1) in ζ . Increases in the ionic strength lead to a pronounced decrease in ζ , the more so the higher the charge number of the counterions, this on account of the term $\exp(-z_1 e\psi/kT)$ in the P.B. equation (eq.I-1,I-6).

Changes in the ζ -potential may further be used to determine the presence and the extent of adsorption. Adsorption of ions changes the surface charge directly, adsorption of neutral substances may lead to a change in the charge as a secondary effect and may also shift the location of the slipping plane.

II-7 APPLICATIONS

At least two types of applications of the theoretical knowledge on electrophoresis may be envisaged, viz. a. the comparison of calculated and experimental values of the mobility, with the aim of obtaining a better understanding of the size and shape of the particle and especially of the quantitative structure of its double layer, and b. the improvement of electrophoretic separations by manipulating the mobilities

7.1 The interpretation of electrophoretic mobility in terms of properties of particles or molecules and of their double layers

The conversion of the electrophoretic mobility into a ζ -potential or an electrophoretic charge can be used to check the validity of certain models of particles or molecules, e g. to check whether the rheology of DNA is sufficiently well described by a cylinder model with a suitably chosen radius. Adsorption of ions changes the charge of the particle and adsorption isotherms can be obtained from electrophoresis. It has been observed that the adsorption of proteins on a variety of particles often changes the electrophoretic mobility from its original value for the bare particles into one very similar to that of the free protein, indicating a shift of the slipping plane to a position comparable to that of the free protein.

Such applications require absolute values of the mobility. Consequently, they cannot be based on paper- or gel-electrophoresis, where electro-osmosis, adsorption of the particles and the influence of tortuosity are hard to quantify. Moreover, a series of values of μ at different compositions of the solution is required to disentangle the influence of the Stern-layer, of adsorption of ions, of the location of the slipping plane, etc

Although this type of application of electrophoresis has led to interesting and useful results, even in the most favorable cases doubts remain, connected with the uncertainty in the location of the slipping plane (cf. Lyklema³⁹).

7.2 Improvement of electrophoretic separations

In electrophoretic separation processes, we use the difference in mobilities between different types of particles. For better separations we are interested in increasing the absolute value of the differences between mobilities, although sometimes the relative differences are also important.

To begin with, we review the essential relations. The mobility is nearly proportional to the ζ -potential with a relatively modest correction for relaxation, largely determined by κ , at least when ζ is not too large. For high ζ and intermediate values of κa , the mobility becomes quite insensitive to ζ . ζ itself increases less than proportionally with the charge, with a very strong influence of κ . Size and shape of the particles have a relatively minor influence on the mobility for a given surface charge density. The temperature affects the mobility mainly through its influence on ϵ and n , but the effect will not be different for different particles.

The particle charge depends strongly on the activity of potential determining ions, in many cases the pH, and occasionally on the specific adsorption of ions, e.g. detergent ions.

Electrophoretic separations are based upon a natural difference in surface charge density and ζ -potential between different types of particles. We want to enhance these differences by a suitable choice of the solution.

Separations are carried out preferably at moderate to low ionic strength, since high ionic strengths combine the drawbacks of low mobilities, high heat production, evaporation and convections.

At moderate ionic strength, say 0.1 M, $1/\kappa$ is about 1 nm, in many cases $\kappa a > 1$, ζ -potentials are fairly low, the mobilities and the differences between them are not very large, but for proteins and other biopolymers a moderate ionic strength corresponds to the natural environment and may be essential for preventing denaturation.

On changing the pH or the activity of other potential determining ions, B, usually one or more fairly narrow regions of pH or pB can be found, where surface charge and potential change rapidly. We mention the region around the pK of acidic or basic surface groups or the region around the p.z.c. of metal oxides, hydroxides, or silver halides. Good conditions for separation are often found near one of the ends of such a region of steep change.

At low ionic strength ζ -potentials and mobilities are higher. In general this leads to larger differences in mobility, but it should be clear from figure 9 that the relaxation effect has a kind of buffering action on the mobilities at high ζ -potentials in a fairly broad range of κa -values. Nevertheless, if other conditions (such as avoiding denaturation) permit, electrophoresis at low ionic strength has the additional advantage of low ohmic losses and thus the possibility of applying high voltages.

In choosing the best circumstances for separation, the qualitative rather than the precise quantitative aspects of the theory are important, but to use these at greatest advantage, the general features and the orders of magnitude involved in the theory should be well understood.

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