

Chapter I

Electric Potentials in Colloidal Systems

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I. Introduction	000	<i>OK as set.</i>
II. General Considerations on the Structure of the Boundary Layer	000	
III. Charge and Potential in the Electrical Double Layer	000	
A. Charge	000	
B. Potential	000	
C. Electrochemical Potential	000	
D. Galvanic Cells	000	
E. Galvani and Volta Potentials; χ -Potential	000	
F. Potential-Determining Ions	000	
G. Oil-Water and Air-Water Interfaces	000	
IV. Ionic Double Layer	000	
A. The Diffuse Double Layer	000	
B. Influence of the Finite Size and Specific Properties of Ions and Other Corrections of the Gouy-Chapman Theory	000	
C. The Double Layer at Curved Interfaces	000	
1. Spherical Interfaces	000	
2. Cylindrical Symmetry	000	
D. Double Layers around Polyelectrolytes	000	
1. Charge and Potential in and around Polyelectrolyte Coils	000	
2. Titration Curves of Polyelectrolytes	000	
V. Electrokinetic Potentials	000	
References	000	

I. INTRODUCTION

Electrophoresis is the movement of charged particles suspended in a liquid, under the influence of an applied electric field. The usual aims of electrophoresis experiments are the obtaining of information on the electrical double layers surrounding the particles, the analysis of a mixture, or its separation into components.

The first aim requires a theory connecting the electrophoretic velocity with fundamental quantities related to the double layer, such as electric potential, charge, and structure. It is the purpose of this chapter to treat the meaning of the notions charge and potential of the double layer, to

show clearly where confusion with relation to these concepts might arise, and to treat their interrelation with electrophoresis and other electrokinetic phenomena.

The theoretical treatment of the electrical double layer depends on its geometry. The most simple case, *viz.*, the double layer at a flat interface will be treated first. With this example, already many facts connected with double layers can be explained. Later in this chapter attention will be paid to more complicated systems: spherical particles, polyelectrolytes, and proteins.

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II. GENERAL CONSIDERATIONS ON THE STRUCTURE OF THE BOUNDARY LAYER

The boundary between two phases is not a mathematical plane, but a layer of finite dimensions. The properties of the two adjacent phases change gradually over a certain distance. These changes depend both on the forces between molecules (van der Waals' forces, purely electrostatic ones, hydrogen bonds, etc.) and on geometrical factors (fitting of the two surface layers onto one another). Even in a one-component system the density and orientation of the molecules change gradually when going, for example, from the liquid to the gas phase. This phenomenon has been treated extensively by Bakker (1) in his theory of capillarity. In a multi-component system the concentrations in the boundary layer are as a rule different from those in bulk, thus leading to what is commonly called *adsorption*.

In most cases the changes near the phase boundary are limited to a very few layers of molecules, but there all properties of the phases are changed, including structure, density, composition, dielectric constant, viscosity, etc. If one or both phases contain ions, the transition layer may be much more extended. In this case it frequently occurs that one type of ion is strongly concentrated at the phase boundary by short-range forces. Ions with a sizable hydrophobic part, like those of detergents, although reasonably soluble in water, will show a tendency to be expelled from the aqueous phase into its boundaries with any less polar phase and so accumulate especially at air-water or oil-water interfaces. Similarly Ba^{++} and SO_4^{--} ions will be more readily adsorbed by BaSO_4 crystals than most other ions because they fit into the BaSO_4 lattice. Many other examples could be given.

But if ions of one sign are adsorbed at the phase boundary, ions of the opposite sign will be attracted by the resulting electric field and accumulate also near the phase boundary. This accumulation of "counterions" (*Gegenions*), however, will be counteracted by their Brownian motion. The result is the formation of an electrical double layer electrically

neutral as a whole which may extend over a thickness of several hundred Ångströms or even more. The structure of this double layer will be treated more completely in the following sections.

Electrophoresis involves a tangential motion of one phase with respect to the other. It occurs only if the two phases carry free charges of opposite sign. Orientation of dipole molecules near the phase boundary, although creating a potential difference between the two phases, cannot give rise to electrophoresis because the charges of the dipole cannot be separated permanently by the applied electric field. So electrophoresis is intimately connected with the ionic part of the electrical double layer and any theoretical approach to electrophoresis has to start with a study of this electrical double layer.

III. CHARGE AND POTENTIAL IN THE ELECTRICAL DOUBLE LAYER

A. Charge

As mentioned above, the total charge of the electrical double layer is zero, but in it ions and electrons may be accumulated preferentially by adsorption. Analytical measurements allow in principle, although not always in practice, the determination of the amount of ions of any kind adsorbed at the phase boundary. Such measurements, however, do not yield any information on the distribution in space of these charge carriers. But quite often relatively simple theoretical considerations come to our aid. If it is known that, for example, electrons and sodium ions are accumulated at the phase boundary between a metal and a salt solution, it is obvious that the electrons are present in the metal phase and the sodium ions in the aqueous phase. We thus consider the metal to be negatively charged with respect to the water phase, the amount of charge being given by the charge of the excess electrons or by the charge of the sodium ions with sign reversed. Further information on the spatial distribution of the charge carriers demands more refined theories such as will be treated in Section IV, Ionic Double Layer.

B. Potential

The spatial distribution of electric charge is of course connected with an electric potential. The exact nature of electric potentials in and near phase boundaries is, however, a subject with numerous pitfalls. Considering the potential difference between two points in space as defined by the amount of work to be done in transferring a given charge from one point to the other, the question immediately presents itself whether this amount of work is independent of the material carrying this charge. We may expect to find the same amount of work involved in the transport of a

hydrogen ion from point *A* to point *B* in an aqueous solution as in the transport of a sodium ion between these same points. But, as soon as a phase boundary is crossed these amounts of work are generally different because, apart from the purely electrostatic work, configurational work, also called chemical work, is performed in changing the immediate surroundings of the sodium (or hydrogen) ion. This configurational work differs for H^+ and Na^+ . Moreover, there are no means of separating the chemical and the electrical work in an unequivocal way, and, as there is no good reason to prefer one charge carrier above the other, it seems as if we do not have any way to determine the electrical work and thus the potential difference between two different phases. The same difficulty, although perhaps to a lesser extent, is valid for the determination of the potential difference between two solutions of different composition.

C. Electrochemical Potential

Guggenheim (2) has repeatedly pointed out the impossibility of separating the chemical and the electrical parts in the work of transporting ions of species *i* and has introduced the notion of *electrochemical potential*, η_i , composed of the *chemical potential*, μ_i , and a term $z_i e \varphi$, where z_i is the charge of the ion and φ the electric potential.

$$\eta_i = \mu_i + z_i e \varphi \quad (1)$$

In any actual transport process only electrically neutral combinations can be transported. In that case the terms $z_i e \varphi$ add up to zero, and for *electro-neutral combinations*

$$\sum_i \eta_i = \sum_i \mu_i \quad (2)$$

Still it is customary to use the notion "potential difference between two phases," and in order to see clearly what this may mean, we shall treat briefly the galvanic cell.

D. Galvanic Cells

The electromotive force (e.m.f.) of a galvanic cell is theoretically well defined; it is closely connected with the total chemical process in the cell [see, Lg. (3)], and measurable in an unequivocal way as the potential difference between the leads connected with the electrodes. These leads are of the same material, and the potential difference measured between them is thus independent of the charge carrier used.

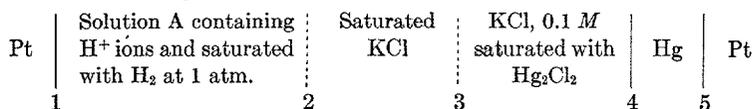
On the other hand, the e.m.f. can be considered as the sum of the potential jumps occurring at each of the phase boundaries in the cell. Although, as shown above, each of these potential jumps separately is inaccessible to measurement, their sum is well defined. It is often possible

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to vary one of the phases in the cell, e.g. by changing the concentrations in a solution, in such a way that of the potential jumps at the phase boundaries involved only one is expected to be seriously affected. In such a case the change in e.m.f. corresponds directly to a change in the potential jump at one single phase boundary.

The cell used for measuring the pH may serve as an example. This cell, which contains five phase boundaries, can be described as follows:



If concentrations in the solution A are varied, only the phase boundaries 1 and 2 are affected. If solution A contains a relatively large amount of a neutral electrolyte, e.g. Na_2SO_4 , and a small concentration of a buffer system, variations in the buffer system will practically not affect the diffusion potential at the liquid junction 2, but they will affect the potential jump between platinum (Pt) and the solution, and this last change is reflected in the change of the e.m.f. of the cell. Written as an equation:

$$\Delta(\text{e.m.f.}) = \Delta(\varphi_{\text{solution}} - \varphi_{\text{Pt}}) \quad (3)$$

With the aid of equation (3) an arbitrary situation may be chosen as a reference point. In a number of cases it is possible to determine the composition of solution A at which the two phases (Pt and A) do not carry free charges. This situation is called the zero point of *charge*, or isoelectric point, and is often taken also as the zero point of *potential* difference between the two phases. Though this may be a useful assumption, it neglects the potential difference that may exist between two phases as a consequence of orientation of dipoles and polarization of atoms in the surface layers.

E. Galvani and Volta Potentials; χ -Potential

Lange and Koenig [(4); see also (5)] have given a clear analysis of the situation. Consider a condensed phase bounded by a vacuum. The electric potential just outside the phase, that is, out of the reach of short-range forces, is independent of the nature of the charge carrier which is used to measure it and consequently practically accessible and well defined. It is called the *Volta potential* (symbol ψ) and plays an important role in electron emission. A survey of methods for measuring Volta potentials was recently given by Möhring (6).

The potential inside the condensed phase has been termed *Galvani potential* (symbol φ) by Lange. It differs from the Volta-potential by an amount χ , the potential jump at the phase boundary:

$$\varphi = \psi + \chi \quad (4)$$

Both φ and χ depend upon the choice of the charge carrier. There are a few theoretical calculations of the potential jump, χ . They assume implicitly the existence of a nonmaterial charge carrier and are essentially calculations of the distribution of nuclei and electrons near the surface. How uncertain they are is shown clearly in the large variation in calculated χ -potentials of water: Verwey (7) found 0.5 volts (water negative) for the boundary water-vacuum. Tpl'yanskiĭ (8) also concluded that the water molecules are preferentially oriented with their positive sides to the surface. Passoth (9), however, found 0.28 volts; Frumkin *et al.* (10), 0.1–0.2 volts; and Hush (11), 0.30 volts—all with water positive with respect to vacuum.

At the phase boundary of two condensed phases we distinguish the two Galvani potentials φ_I and φ_{II} and their difference $\chi_{I, II}$.

$$\chi_{I, II} = \varphi_I - \varphi_{II} \quad (5)$$

The interfacial potential jump $\chi_{I, II}$ is not equal to $\chi_I - \chi_{II}$ because the molecules of both phases are rearranged at the interface as a consequence of the contact between the phases (Fig. 1). Frequently $\chi_{I, II}$ is divided into

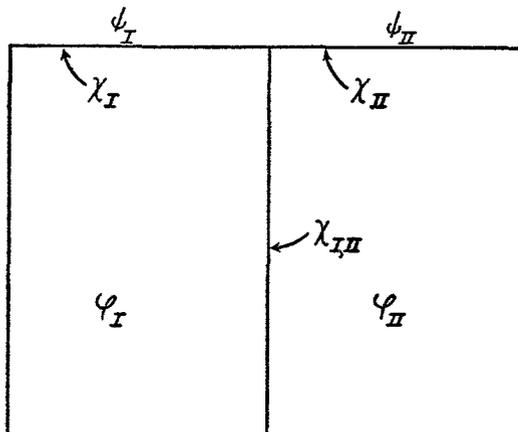


FIG. 1. Diagram illustrating Galvani (φ), Volta (ψ), and χ -potentials.

two contributions: one to be called $D_{I, II}$ and based upon the distribution of free charges, and the other to be called χ (the χ -potential in the restricted sense) and connected with polarizations and orientations of neutral molecules. At the zero point of charge $D_{I, II} = 0$, but χ usually has a finite value.

F. Potential-determining Ions

If ions of type i occur in both phases and equilibrium exists, the electrochemical potential η_i , of these ions has the same value throughout the whole system:

$$\eta_i^I = \eta_i^{II} \quad (6)$$

or, with equation (1):

$$\mu_i^I + z_i e \varphi^I = \mu_i^{II} + z_i e \varphi^{II} \quad (7)$$

Assuming phase II to be a solid with fixed composition (pure metal, oxide, sulfide, halide, etc.) and phase I to be a solution, dilute with respect to the ions (i), μ_i^{II} is a constant, and

$$\mu_i^I = (\mu_i^I)_0 + kT \ln c_i \quad (8)$$

where $(\mu_i^I)_0$ is the standard potential of i ions, c_i their concentration in the bulk of phase I, and k the Boltzmann constant.

Substituting this in equation (7) we obtain the Nernst equation (9), which is seen to be valid not only for the potential difference between a metal and a solution, but also for oxides or salts in equilibrium with solution.

$$\varphi^I - \varphi^{II} = \text{constant} + \frac{kT}{z_i e} \ln c_i = \text{constant} + \frac{RT}{z_i F} \ln c_i \quad (9)$$

The ions of type i , for which equation (9) is valid, have been called *potential-determining ions* by Lange and Koenig (4). The Ba^{++} and SO_4^{--} ions in the system BaSO_4 -solution, cited in Section II above, are examples of type i .

The χ -potential (in the restricted sense) is only based upon short-range forces. It may therefore be assumed to be independent of the distribution of free charges near the interface. With this assumption, the double-layer potential $D_{I, II}$ is found also to obey a Nernst equation:

$$D_{I, II} = \varphi^I - \varphi^{II} - \chi = \text{constant} + \frac{RT}{z_i F} \ln c_i \quad (10)$$

If the concentration of i ions is not very small, deviations from the simple logarithmic equation appear. It is customary to correct for these deviations by introducing an activity coefficient in the logarithmic term, but it should be realized that part of the deviations may just as well be attributed to the liquid junction.

G. Oil-Water and Air-Water Interfaces

Let us consider the distribution of an electrolyte (monovalent for simplicity) between two immiscible liquid phases (further denoted as oil and water) in equilibrium. Equality of the electrochemical potentials of the ions in both phases leads to

$$\eta_+^{\text{oil}} = \eta_+^{\text{w}}$$

or:

$$(\mu_+^{\text{oil}})_0 + kT \ln c_+^{\text{oil}} + e\varphi^{\text{oil}} = (\mu_+^w)_0 + kT \ln c_+^w + e\varphi^w \quad (11)$$

and

$$\eta_-^{\text{oil}} = \eta_-^w$$

or:

$$(\mu_-^{\text{oil}})_0 + kT \ln c_-^{\text{oil}} - e\varphi^{\text{oil}} = (\mu_-^w)_0 + kT \ln c_-^w - e\varphi^w \quad (11a)$$

By subtracting the two equations (11) and (11a) from each other and taking into account that $c_+ = c_-$, one finds:

$$\varphi^{\text{oil}} - \varphi^w = \frac{(\mu_+^w)_0 - (\mu_+^{\text{oil}})_0 + (\mu_-^{\text{oil}})_0 - (\mu_-^w)_0}{2e} \quad (12)$$

The Galvani potential difference is independent of the concentration of electrolyte.

When the nonaqueous phase is a nonpolar hydrocarbon oil or air, the electrolyte concentration in it is zero or is so small as not to be sufficiently well defined to influence the potential difference. The distribution of charge and potential in the aqueous side of the boundary is in that case governed by the difference in adsorption of the two kinds of ions at the interface.

Incidentally the air-water interface is a good example of the determination of the Volta potential [see e.g. reference (12)]. If one electrode is placed in the air close to the surface and a second one connected by means of a saturated KCl liquid junction to the aqueous solution, the potential difference between these two electrodes changes parallel to the Volta potential of the solution. Adsorption of surface-active electrolytes and nonelectrolytes and spreading of amphipolar substances changes the Volta potential markedly. This change in Volta potential is equal to a change in the total χ -potential as the Galvani potential may be assumed to be unaffected by the small concentrations involved. The χ -potential at the water-air interface usually contains contributions from oriented dipoles and also from free ions.

IV. IONIC DOUBLE LAYER

As stated in Section II, electrophoresis occurs only in the presence of freely mobile charges. It is highly sensitive to the amount and spatial distribution of these charges. Oriented dipoles and polarized molecules, giving rise to the χ -potential jump, do not lead to electrophoresis and for our problems are important only insofar as they influence the distribution of free charges in the ionic layers.

Our next aim will therefore be a closer study of the ionic double-layer potential $D_{I, II}$. Not to complicate matters unnecessarily, we shall provisionally consider only double layers at flat (noncurved) interfaces,

A. The Diffuse Double Layer

The ionic double layer consists of two layers of charges of opposite sign. In most cases one of the layers is localized in a plane at the transition between the phases, whereas the other one has the character of a space charge, extending fairly far into one of the two phases.

In the mathematical treatment the first-named layer is usually represented as smeared out in a mathematical plane. This is not as crude an approximation as it might seem to be, for often the surface charge is carried by electrons or by potential-determining ions. They are not localized, so that one might say that the excess charge is shared more or less equally between all electrons or potential-determining ions near the interface.

In the beginning of the development of the double-layer theory, the countercharge was represented as a space charge (extension not specified) in Helmholtz' treatment of electrokinetics (13), as a surface charge by Perrin (14), and again as a space charge, carried by dimensionless ions, by Gouy (15) and by Chapman (16). Their treatment still furnishes the basis of modern double-layer studies. Stern (17), Grahame (18), and others have refined the Gouy-Chapman treatment by introducing finite size, hydration, etc., of the ions. We shall first follow the Gouy-Chapman treatment. A schematic picture of their double-layer model is given in Fig. 2, showing

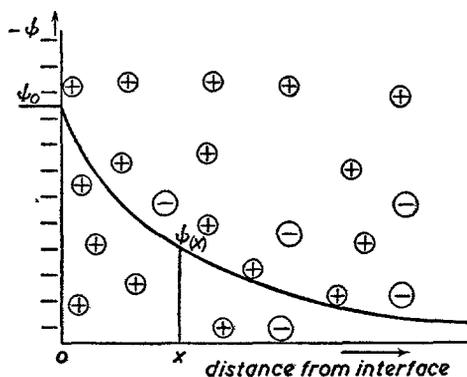


FIG. 2. Distribution of ions and potential in the diffuse double layer, omitting the χ -potential jump.

at the same time the potential distribution. The χ -potential jump, which ought to be superimposed on the double-layer potential as a sharp jump near the interface, has been omitted; the surface charge is assumed to be negative. Positive ions are attracted to the surface, negative ones are pushed away. The average number of ions (\bar{z}) per unit volume at a distance

(x) from the interface $n_i(x)$ is connected with the average potential $\psi(x)$, by a Boltzmann equation:

$$n_i(x) = n_i(\infty) \exp\left(-\frac{z_i e \psi(x)}{kT}\right) \quad (13)$$

where $n_i(\infty)$ is the number of ions in the bulk of the solution.

In the treatment of properties of strong electrolytes where equation (13), is also used, it has been criticized by Fowler and others (19); see also: Onsager (20), Kramers (21), Fowler and Guggenheim (22), and especially Kirkwood (23). The objection is that in the exponential $z_i e \psi(x)$ ought to be the work done in bringing an ion to the distance (x). However, if it is known that the ion is at x , it will influence the distribution of the ions in its neighborhood, so that the potential at (x) will deviate from the mean potential $\psi(x)$. Casimir (24) has pointed out that application of equation (13) is justified when large particles or charged surfaces with very many elementary charges are considered and when the electrolyte concentration is not too high. The objections are quite valid in the theory of electrolytes, where double layers (ionic atmospheres) around separate ions are considered.

The potential distribution in the double layer is connected with the space charge, $\rho(x)$, by Poisson's equation (14). This equation is the mathematical equivalent of the physical picture that $4\pi/\epsilon$ lines of force emanate from an electrostatic unit of charge in a medium with dielectric constant ϵ .

$$\text{div} [\epsilon \text{grad } \psi(x)] = -4\pi\rho(x) \quad (14)$$

If we assume ϵ to be a constant (see, however, below) and remember that in our model $\psi(x)$ changes only in the x -direction, equation (14) takes the simple form:

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi\rho(x)}{\epsilon} \quad (15)$$

The charge density is built up from the ionic charges or:

$$\rho(x) = \sum_i z_i e n_i(x) \quad (16)$$

The relations (13), (15), and (16) can be combined into the so-called Poisson-Boltzmann equation (17), which forms the basis of the double-layer theory:

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi}{\epsilon} \sum_i z_i e n_i(\infty) \exp\left(-\frac{z_i e \psi(x)}{kT}\right) \quad (17)$$

In the Debye-Huckel theory of strong electrolytes the analogous equation is solved by expanding the exponentials, retaining only the first two

terms. This is a reasonable approximation provided $z_+e\psi(x)/kT < 1$ or $\psi(x) < 25/z_+$ millivolts at room temperature. Applying this approximation, and taking into account the electroneutrality far from the interface

$$\sum z_i e n_i(\infty) = 0 \quad (18)$$

equation (17) is transformed into:

$$\frac{d^2\psi(x)}{dx^2} = \kappa^2\psi(x) \quad (19)$$

in which

$$\kappa^2 = \frac{4\pi e^2 \sum_i n_i(\infty) z_i^2}{\epsilon kT} \quad (20)$$

The solution of equation (19)

$$\psi(x) = \psi(0) \exp(-\kappa x) \quad (21)$$

shows that $1/\kappa$ has the dimension of a length and denotes that value of x for which $\psi(x) = \psi(0)/e$. Therefore $1/\kappa$ is a good measure for the extension of the double layer and is often called "thickness of the double layer."

In colloidal systems the application of the Debye-Hückel approximation (19) is frequently not justified. In the first place the underlying assumption $z_+e\psi(x)/kT < 1$ is mostly not fulfilled in the major part of the double layer. Potentials in the double layer may be as high as several hundred millivolts. Secondly, experiments on electrophoresis and on the stability of colloids reveal a pronounced difference between the influence of positive and negative ions. In equations (19) and (20), however, they appear in a completely symmetrical way, whereas the complete exponentials of equation (17) are indeed quite asymmetric with respect to positive and negative values of $z\psi_0$. It is therefore necessary to make use of the complete equation (17) for colloidal systems.

A first integration may be carried out after multiplying both sides of equation (17) by $\frac{2d\psi(x)}{dx}$. Making use of the boundary conditions

$$\psi(\infty) = 0 \quad \text{and} \quad \left(\frac{d\psi(x)}{dx}\right)_{x=\infty} = 0$$

integration leads to

$$\left(\frac{d\psi(x)}{dx}\right)^2 = \frac{8\pi kT}{\epsilon} \sum_i n_i(\infty) \left(e^{-\frac{z_i e \psi(x)}{kT}} - 1\right) \quad (22)$$

or for a solution of a $z_+ - z_-$ valent electrolyte

$$\frac{d\psi(x)}{dx} = \mp \sqrt{\frac{8\pi n kT}{\epsilon z_+ z_-}} \sqrt{z_- e^{-\frac{z_+ e \psi(x)}{kT}} + z_+ e^{\frac{z_- e \psi(x)}{kT}} - z_+ - z_-} \quad (23)$$

where $n = z_+n_+(\infty) = z_-n_-(\infty)$ is the concentration expressed in elementary charges per unit volume. The plus sign is valid for a negatively charged surface, the minus sign for a positive surface.

For a symmetrical $z - z$ valent electrolyte equation (23) can be written:

$$\frac{d\psi(x)}{dx} = -\sqrt{\frac{8\pi nkT}{\epsilon z}} \left\{ e^{\frac{z\epsilon\psi(x)}{2kT}} - e^{-\frac{z\epsilon\psi(x)}{2kT}} \right\} \quad (24)$$

The condition of electroneutrality in the whole system requires that any plane parallel to the interface cut the double layer into two layers carrying equal but opposite charges. Calling the sum of the surface charge σ at the interface and the space charge between $x = 0$ and x , $\sigma(x)$, this condition leads to

$$\sigma(x) = -\int_x^\infty \rho(x) dx \quad (25)$$

Using the Poisson equation (15) to substitute for $\rho(x)$ and carrying out the integration we find:

$$\begin{aligned} \sigma(x) &= +\int_x^\infty \frac{\epsilon}{4\pi} \frac{d^2\psi(x)}{dx^2} dx = -\frac{\epsilon}{4\pi} \frac{d\psi(x)}{dx} \\ &= \pm \sqrt{\frac{\epsilon nkT}{2\pi z_+ z_-}} \sqrt{z_- e^{-\frac{z_+ \epsilon \psi(x)}{kT}} + z_+ e^{+\frac{z_- \epsilon \psi(x)}{kT}} - z_+ - z_-} \end{aligned} \quad (26)$$

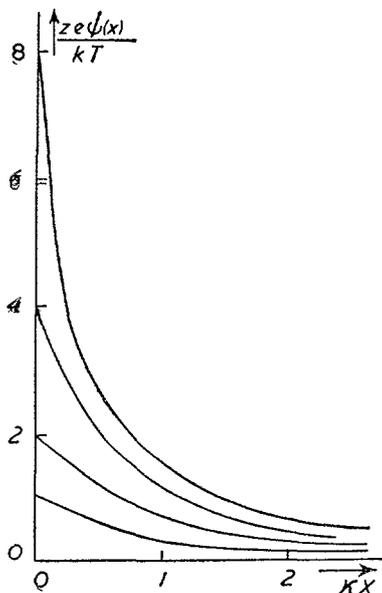


FIG. 3. Potential in the diffuse double layer for various surface potentials and symmetrical $z-z$ valent electrolytes as a function of the distance from the interface.

an equation which for $x = 0$ relates the surface charge $\sigma = \sigma(x = 0)$ with the surface potential $\psi_0 = \psi(x = 0)$.

Although a second integration of equation (23) can be carried through, at least when z_+ and z_- are equal or not larger than 2, the resulting equations are rather complicated and will not be needed here. Figure 3 gives a graphical representation of the potential as a function of the distance from the interface. In this figure the dimensionless units $ze\psi/kT$ and κx are used, which means, that the potentials are expressed in units of $25/z$ millivolts and the distances in units $1/\kappa$. The values of $1/\kappa$ can be calculated from equation (20). For water at 25°C. and symmetrical $z - z$ valent electrolytes, this equation can be written: $1/\kappa = 96/z\sqrt{c}$ in which $1/\kappa$ is expressed in Ångström units and c in millimoles per liter. For monovalent electrolytes, $1/\kappa$ is about 10 Å. for 0.1 molar, 100 Å. for millimolar, and 1000 Å. for 10^{-5} molar solutions.

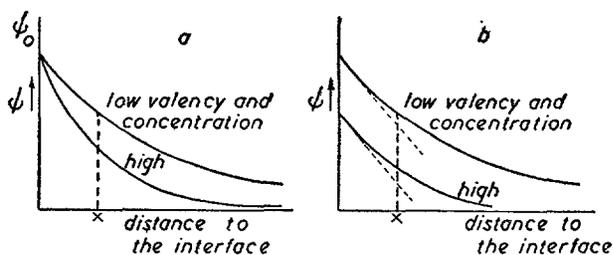


FIG. 4. The part of the double layer that is responsible for electrophoresis becomes less important for higher concentration and valence of electrolyte. a. Constant surface potential. b. Constant surface charge.

The fact that the double layer is thinner and the potential drop steeper in more concentrated solutions and in solutions containing ions of higher valency than in dilute ones is of great importance for electrophoresis. There are many indications that in electrophoresis the first few layers of molecules near the interface do not move and that electrophoresis is determined by the outer part of the double layer. Figure 4 shows schematically how, for constant surface potential and (still more pronounced) for constant surface charge, the potential at a distance x from the interface is lower, the thinner the double layer. Consequently electrophoresis will be slower, the higher the ionic strength.

Experimental checks of the double layer theory are usually based upon the relation between surface charge and potential (equation 26). Extensive data on the interface mercury-aqueous solution are available through electrocapillary work (18) and on the interface AgI-aqueous solution by determination of the adsorption of potential-determining ions (I^- , Ag^+)

combined with potential measurements on a cell with a silver-silver iodide electrode (25, 26). Double layers on many other materials have been investigated.

Equation (26) turns out to be valid only for low concentrations of electrolyte, low potentials, and low charges. For higher charges equation (26) predicts an exponential relation between charge and potential, whereas a more nearly linear relation is found. This discrepancy may be ascribed to the finite size of the ions as was first clearly recognized by Stern (17). Even at a concentration in the bulk of the solution as low as $\frac{1}{100}$ molar and a surface potential of 250 millivolts (mv), which is not extremely high, the concentration of counterions near the surface is, according to the Boltzmann equation,

$$\text{Conc. at surface} = c_{\infty} \exp\left(\frac{e\psi}{kT}\right) = \frac{1}{100} \exp \frac{250 \text{ mv}}{25 \text{ mv}} = 220 \text{ molar}$$

—clearly an impossible value. For the innermost parts of the double layer, the Boltzmann equation can obviously not be accepted without considerable corrections.

B. Influence of the Finite Size and Specific Properties of Ions and Other Corrections of the Gouy-Chapman Theory

In the preceding paragraph it has been shown that the finite size of ions necessitates corrections of the diffuse double-layer theory. These corrections are much more important near the interface, where concentrations may be high, than in the bulk of the solution. Stern (17) was the first to introduce a correction of this kind by treating the adsorption of the first layer of ions separately and using the Gouy-Chapman theory for the remaining part of the double layer. In the first layer, electrical effects, size of the ions, and specific adsorption could be taken into account, thus forming a basis for the explanation of specific differences between ions of the same valence in their influence on electrophoresis, double-layer capacity, etc. A fine elaboration of Stern's ideas was given by Grahame (18).

The Russian school (27-30) paid attention to the influence of the discreteness of the charges in the Stern layer on the amount of specifically adsorbed ions and the accompanying potential distribution. Recently their results were confirmed and extended by Grahame (31, 32).

Bikerman (33) applied a number of corrections to the Boltzmann equation, one of them for ionic volume, thus automatically cutting out the absurdly high concentrations that may occur in the Gouy-Chapman formula. In addition he considered specific adsorption for the first layer of ions.

Parsons (34), while using the Stern approach, showed that the specifi-

27

ally adsorbed ions follow an Amagat equation rather than a Langmuir one. Loeb (35) and Williams (36) took the Debye-Hückel interaction between the individual ions in the double layer into account.

Freise (37) treated the diffuse double-layer structure from the point of view of ideal mixing and found deviations from the Gouy-Chapman theory which could be interpreted as a consequence of the finite size of solvent molecules and ions.

Conway *et al.* (38), Hasted and co-workers (39), Grahame (40), and Booth (41) considered the dielectric constant in the double layer. From their investigations it appeared that the dielectric constant may be considerably lowered in the strong electric field in the double layer. This change in dielectric constant has, however, a relatively minor influence on the relation between surface charge (σ) and surface potential ψ_0 . Bolt (42) concluded that most of the corrections in the diffuse part of the double layer are mutually compensating, so that for many practical purposes they may be neglected.

This, however, is not the case for the correction for finite size and specific adsorption of the first layer of ions. For these effects we shall apply the Stern treatment as modified by Grahame.

The surface charge is again assumed to be smeared out in a mathematical plane. The first layer of ions in the solution is found at a distance δ from this plane. Beyond δ the double layer follows the Gouy-Chapman pattern. In Stern's own treatment there is some uncertainty as to how the first layer of ions and the diffuse double layer connect with each other. Grahame distinguishes two planes in the double layer, parallel to the surface, which he denotes as the inner and the outer Helmholtz plane. The outer Helmholtz plane lies at the distance of closest approach to the surface for hydrated ions, still belonging to the diffuse double layer. In the absence of specific adsorption, no centers of ions occur between the outer Helmholtz plane and the surface charge. The inner Helmholtz plane is the plane in which specifically adsorbed and presumably dehydrated ions are found. The distribution of ions and the course of the potential according to Grahame's picture are given schematically in Fig. 5, a for negative surface charge without specific adsorption. Figure 5, b and c, shows the situation as modified in the presence of weak and strong specific adsorption of anions. In the last case, the specific adsorption is so strong, that not only the charge of the diffuse layer is positive but also that of the wall. Figure 5, d and e, shows cases with specific adsorption of cations. With strong adsorption of cations, the charge in the diffuse double layer may become reversed and electrophoresis would be directed to the negative pole.

Quantitative treatment of the case without specific adsorption is rather simple. The double layer may be represented by a system of two condensers

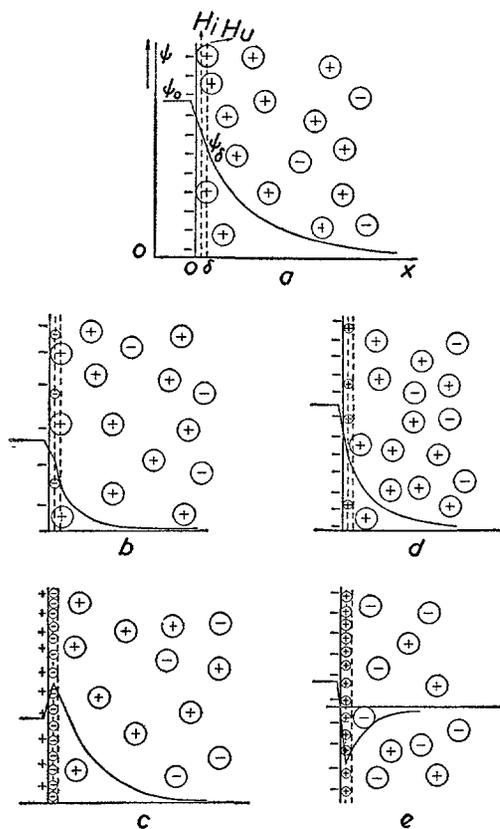


FIG. 5. Distribution of ions and potential in the double layer according to Grahame (18). a. No specific adsorption. b. Specific adsorption of anions. c. Strong specific adsorption of anions. d. Specific adsorption of cations. e. Strong specific adsorption of cations.

in series. The first one, the "molecular condenser," has the plane of the charge on the wall as one of its plates and the plane δ as the other one. Its capacity can be written as:

$$C_m = \frac{\epsilon'}{4\pi\delta}$$

where ϵ' is the effective dielectric constant in this layer. The diffuse double layer has a capacity

$$C_d = \frac{\sigma}{\psi(x = \delta)}$$

in which $\sigma = \sigma_d$ (no charges between $x = 0$ and $x = \delta$). The total capacity

C is found from

$$\frac{1}{C} = \frac{1}{C_m} + \frac{1}{C_d} \quad (27)$$

and is also equal to the ratio of surface charge (σ) to total potential drop (ψ_0).

The capacity of the diffuse part of the double layer can be calculated as a function of the double layer charge σ by means of equation (26). For low charge it is equal to $\epsilon/4\pi \frac{1}{\kappa}$, but it increases strongly with increasing potential.

Stern considered the capacity of the molecular condenser as a constant, but Grahame has shown that it can be more satisfactorily treated as a function of the surface charge, i.e. as a function of the field strength near the surface. In order to determine C_m , Grahame (18, 43) applied equation (27) to the double layer on mercury in aqueous NaF solutions. When the electrolyte concentration is high, the diffuse part of the double layer is thin ($1/\kappa$ small) and possesses a high capacity. Consequently, according to equation (27) the total capacity is mainly determined by C_m . For this reason Grahame used the total capacity of the double layer in 1 *M* NaF to calculate C_m . Figure 6 shows the result obtained. Conversely with the

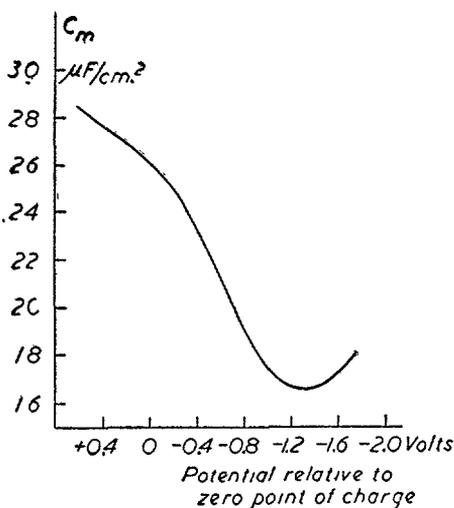


FIG. 6. Capacity of the molecular condenser on mercury in 1.0 *M* NaF solutions.

aid of C_m thus found, the total double-layer capacity in lower concentrations of NaF can be calculated, supposing C_m independent of the electrolyte concentration.

In this way excellent agreement with experiments is obtained. Figure 7 shows the calculated and experimental results for 0.001 *M* NaF.

Grahame (44) determined data for many other electrolytes. Similar results have been obtained for the double layers on mercury in water by Ross McDonald (45), G. and E. Darmais (46), Vorsina and Frumkin (47),

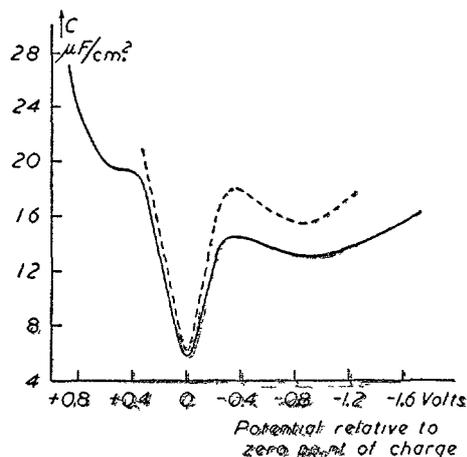
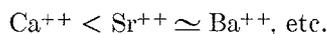


FIG. 7. Total capacity of the double layer on mercury in 0.001 *M* NaF. Dashed line calculated with equation (27). Solid line based on experiments (18, 43).

Watanabe *et al.* (48); on AgI in water, by Overbeek and Mackor (49, 50), and Lijklema (26); on Ag₂S in water, by Freyberger and de Bruyn (51) and Iwasaki and de Bruyn (52).

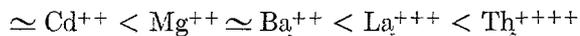
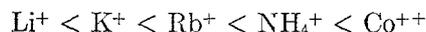
The picture so far developed already includes some specific effects. The capacity of the molecular condenser (Stern layer) is expected to be dependent on size and polarizability of the ions, and thus to follow the lyotropic order.

According to Grahame's data on mercury the capacity of the molecular condenser increases systematically with atomic number and valence (that is in the lyotropic order) (53):



The differences in capacity between different ions are so small that they are distinguishable only with very accurate experiments.

Lijklema's work on AgI shows the following order for the cations



and for the anions



The effects on AgI, though still small, as shown for instance in Fig. 8, are somewhat greater than those on mercury.

Although specific adsorption of ions is of rather common occurrence, there are only very few cases where a quantitative interpretation has been

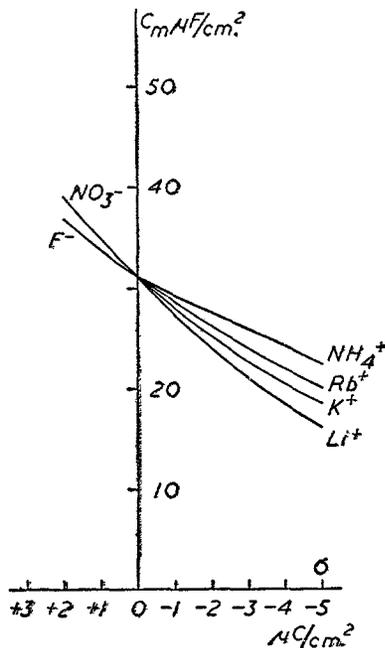


FIG. 8. Capacity of molecular condenser on silver iodide according to Lijklema (26).

made. A good example is the adsorption of Cl^- on mercury as investigated by Grahame (18). If the mercury is sufficiently negative no adsorption of Cl^- takes place (because it is repelled too strongly by the electric field). But even with a weak negative charge on the mercury, Cl^- is already adsorbed specifically; on positively charged mercury the Cl^- adsorption is so strong that the charge of the diffuse double layer is also positive (see Fig. 5c). This strong specific adsorption of Cl^- (and other halides) on mercury is obviously related to the strong interaction between mercury and halides in mercury halides.

Very obvious examples of specific adsorption are found in those cases where adsorbed ions invert the sign of the charge in the diffuse double layer. Many complex ions (Co-, Pt-complexes) and paraffin-chain ions

have this property. In this connection it should be borne in mind that such a charge reversal can never be brought about by purely electrostatic forces.

Paraffin-chain ions are specifically adsorbed at all interfaces between water and other phases because the paraffin tail is "squeezed out" as a consequence of the strong attractions among the water dipoles. This effect is particularly evident at water-"oil" interfaces, where by "oil" we mean any nonpolar or slightly polar organic liquid.

In the simplest cases the potential difference between water and oil is determined by the distribution of an electrolyte between the two phases (as treated in Section III, G, equations (11 and 12)). In such circumstances there will be a diffuse double layer in each of the phases and no surface charge at all at the phase boundary [see Verwey and Niessen (54)]. Quite often the concentration of ions in the oil phase will be very low, and the amount of charge in the double layer very small as well. Even a relatively weak specific adsorption of ions at the interface will change the picture to the familiar one of a surface charge at the phase boundary and a space charge on its aqueous side.

An interpretation of the capacity of the molecular condenser in terms of dielectric constant and distance between the layers of charges is as yet hardly possible. A normal value for this capacity is $20 \mu\text{F./cm.}^2$. With $\epsilon' = \epsilon = 80$ this would correspond to a distance δ of 35 \AA . and with $\epsilon' = 2$ to $\delta = 1 \text{ \AA}$. Both values are quite improbable, and the truth lies somewhere in between—probably at a dielectric constant of 4 to 10 and a distance of 2-5 \AA .

The lyotropic order for monovalent ions corresponds to a stronger hydration for the smaller ions. Strong hydration implies at the same time a high effective ionic radius (high value of δ) and a small dielectric constant, both factors working in the direction of a small capacity. The large capacity for polyvalent ions is more difficult to interpret. Among other effects one should take into consideration that the lines of force spreading from a polyvalent ion hit the interface on a larger area than those of a monovalent ion. The lines of force will therefore pass regions relatively far from any ion, where the water molecules are relatively free and the dielectric constant is high.

This discussion shows that interpretation of the capacity of the molecular condenser is connected with orientation and fixation of molecules very near the interface. Mackor (25) has pointed out that an equally valid interpretation is based on variability of the χ -potential. Indeed the seat of at least a part of the χ -potential is in the same layers of molecules that form the dielectric for the molecular condenser. It is more a question of convenience than one of principle how the contribution of these molecules

to the electric field is split up between their influence on the χ -potential and on the dielectric constant of the molecular condenser. Mackor's way of interpretation has the advantage that the dissymmetry in the capacity at the two sides of the zero point of charge, which is nearly always found, can be related to a preferential orientation of the water molecules at the uncharged surface. More obvious cases of a shift of the χ -potential are found in the influence of electroneutral materials (acetone, urea, thiourea, resorcinol) on double-layer properties. In preferential adsorption at the interface such materials are as a rule oriented, thus causing an extra potential difference between the two phases and a corresponding shift in the zero point of charge. For example the zero point of charge for AgI in water moves in the direction of lower I^- concentrations by addition of acetone (55).

C. The Double Layer at Curved Interfaces

In actual electrophoresis of finite particles the interface between particle and medium cannot be completely flat. But if the radius of curvature of the interface is much larger than the thickness of the double layer ($1/\kappa$), the treatment of the double layer at a flat interface (as given above in Section IV, A and B) forms a very good approximation. However, for small particles with a size of the same order as the thickness of the double layer or even smaller, an explicit treatment of the double layer at curved interfaces is desirable. There is a good deal of literature on spherical double layers and a few articles on cylinders. It is typical for these cases that there is relatively more volume available far away from the interface than close to it. Consequently, those parts of the double layer where the potential is low are relatively more important than the flat double layer and the Debye-Hückel approximation is more successful for curved double layers than for flat ones. Going on to particles with a very small radius, this same effect explains the success of the Debye-Hückel theory for electrolytes, although potentials at the ionic surfaces are frequently higher than 100 millivolts.

1. Spherical Interfaces

The Poisson-Boltzmann equation (17)

$$\operatorname{div} \operatorname{grad} \psi(r) = -\frac{4\pi e}{\epsilon} \sum_i n_i(\infty) z_i \exp\left(-\frac{z_i e \psi(r)}{kT}\right) \quad (17) \quad (17')$$

takes the following form for spherical symmetry

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi(r)}{dr} \right) = -\frac{4\pi e}{\epsilon} \sum_i n_i(\infty) z_i \exp\left(-\frac{z_i e \psi(r)}{kT}\right) \quad (28)$$

For low potentials Debye and Hückel (56) have given the following approximated solution of equation (28):

$$\psi(r) = \psi(a) \frac{a}{r} e^{\kappa(a-r)} \quad (29)$$

in which a denotes the radius of the sphere. The surface charge density σ is then given by

$$\sigma = -\frac{\epsilon}{4\pi} \left(\frac{d\psi(r)}{dr} \right)_{r=a} = -\frac{\epsilon\psi(a)}{4\pi a} (1 + \kappa a) \quad (30)$$

and the total charge on the spherical particle by:

$$Q = 4\pi a^2 \sigma = -\epsilon a \psi(a) (1 + \kappa a) \quad (31)$$

Just as in the case of flat double layers it is insufficient for most purposes to use only the first two terms of the power series and it is desirable to find more precise solutions of the Poisson-Boltzmann equation (28). However, an integration of the total spherical Poisson-Boltzmann equation in closed form is not possible. Various useful elaborations are given in the literature. In 1928 Müller (57) elaborated a procedure for numerical integration of equation (28), or rather of the special form it takes for symmetrical electrolytes. The number of solutions that have been worked out, however, was insufficient to make the method of much practical value.

Gronwall *et al.* (58) and La Mer *et al.* (59) gave a solution of equation (28) in the form of a series expansion in terms of the dimensionless quantity $z^2 e^2 / \epsilon a k T$ for $z - z$ valent electrolytes. Unfortunately only the first few terms of the series have been calculated, the series converging only for low values of the parameter; solutions based on these terms therefore are acceptable only in cases of still rather low surface charge and potential.

Mikulin (60) has shown that replacement of κ by $(\kappa + \text{constant} \cdot \psi)$ in equation (29) leads to an approximate solution of the complete Poisson-Boltzmann equation of rather wide acceptability. The method, however, is rather laborious and still not quite exact.

The most practical way to solve equation (28) is found in the use of electronic computers. This amounts to mechanizing the tedious procedure of numerical integration so that solutions for a sufficient number of conditions can be evaluated. Hoskin (61) introduced this method. His results were for the greater part confirmed and extended by Loeb and associates (62). The computer calculations by Wall and Berkowitz (63) on polyelectrolytes (see Section IV, D) also contain data on spherical double layers for high potentials. Hoskin's data cover the values $ze\psi_0/kT = 1, 2, 4, 6, 8$ and $\kappa a = 1, 3, 5, \text{ and } 15$. Loeb *et al.* extend these data to higher potentials and smaller values of κa and give accurate approximations for combinations of parameters not covered by the actual computations.

By way of illustration we include Table I, taken from the work of Loeb *et al.* (62), giving the surface charge density σ as a function of $ze\psi_0/kT$ and κa .

A practical application of Hoskin's data can be found in the work of Stigter and associates (64, 65) on surface potential, charge, and other properties of soap micelles. Surface potentials appear to vary between 100 and 200 millivolts. Application of the Debye-Hückel expression would erroneously lead to potentials more than twice as high in several cases.

Combinations of diffuse double-layer theory around spherical particles, with Stern corrections are as yet rarely used, but it is felt that in any case of practical interest, the quasi-flat Stern (or Grahame) molecular condenser may be combined with the spherical diffuse layer, because the thickness of the Stern layer is so small ($\delta \ll a$).

2. Cylindrical Symmetry

The distribution of ions in a diffuse double layer around a cylindrical particle has been treated for the case of small potentials by Dube (66) and by Gorin (67). Charge and potential are related through Bessel functions.

Fuoss *et al.* (68) have treated the case of infinitely thin rods surrounded by diffuse double layers consisting only of ions with a charge opposite to that of the rods themselves. The case is important for the behavior of polyelectrolytes.

D. Double Layers around Polyelectrolytes

In the preceding sections we mainly considered systems in which the surface charge is generated by *adsorption*. There are other very important colloids in which the charge is formed by *dissociation*. These are nowadays called polyelectrolytes, but they are more or less identical with what used to be called hydrophilic colloids. Polyelectrolytes are molecules of colloidal dimensions containing a large number of ionizable groups like

$-\text{COOH}$, $-\text{NH}_2$, $\text{>P}=\text{O}$, etc. Proteins are an example of this group.

One might be inclined to consider H^+ and OH^- as the potential-determining ions for these systems. The Nernst equation (9), however, is not followed exactly because the particles cannot take up an indefinite amount of H^+ ions and saturation plays a role. Or, more formally, the chemical potential of the H^+ ions on the particles is not a constant but depends on the number already adsorbed.

The relation between charge and pH can be found experimentally by titration. Titration curves are more complicated than those of simple

two separate
bonds if
possible:
 $\text{>P}=\text{O}$
 $\text{>P}-\text{OH}$

TABLE I

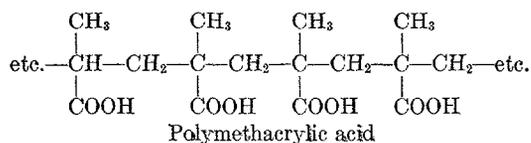
VALUES^a OF $\frac{4\pi e}{ekT} \frac{z}{\kappa} \sigma$ FOR VARIOUS VALUES OF κa AND $\frac{ze\psi_0}{kT}$

$\frac{ze\psi_0}{kT}$	$\kappa a = 20$	$\kappa a = 10$	$\kappa a = 5$	$\kappa a = 2$	$\kappa a = 1$	$\kappa a = 0.5$	$\kappa a = 0.2$	$\kappa a = 0.1$
1	1.0913	1.1403	1.2386	1.5344	2.0297	3.0238	6.0155	11.010
2	2.4430	2.5359	2.7230	3.2910	4.2522	6.2019	12.132	22.087
3	4.3861	4.5144	4.7740	5.5698	6.9372	9.7562	18.495	33.322
4	7.4067	7.5614	7.8714	8.8428	10.530	14.080	25.376	44.896
5	12.271	12.444	12.791	13.878	15.785	19.878	33.310	57.170
6	20.218	20.403	20.772	21.929	23.965	28.377	43.327	70.864
7	33.273	33.465	33.848	35.041	37.138	41.678	57.395	87.544
8	54.773	54.967	55.359	56.569	58.677	63.214	79.008	110.34
9	90.202	90.397	90.791	92.013	94.106	98.580	113.95	144.95
10	148.60	148.80	149.20	150.42	152.50	156.87	171.58	201.08
11	241.89	245.09	245.48	246.70	248.77	253.03	267.09	294.58
12	403.63	403.83	404.23	405.44	407.49	411.68	425.18	450.71
13	665.34	665.53	665.94	667.14	669.17	673.33	686.38	710.29
14	1096.8	1097.0	1097.1	1098.6	1100.6	1104.8	1117.5	1140.2
15	1808.2	1808.4	1808.8	1810.0	1812.0	1816.1	1828.6	1850.5
16	2981.2	2981.4	2981.8	2983.0	2985.0	2989.0	3001.3	3022.5

^a Computed by Loeb *et al.* (62).

electrolytes, mainly on account of the mutual interaction amongst the charged groups.

Consider a polyelectrolyte molecule with carboxyl groups. The dissociation of the first few groups will give the molecule a negative charge, which will hamper the dissociation of the following groups. The carboxyl groups become more weakly acidic, the higher the degree of ionization. As the interaction between different charged groups is partly screened off by the ionic atmospheres around each of them, the interaction depends on the ionic strength of the solution and consequently titration curves change with ionic strength. At a fixed pH dissociation is stronger, the higher the salt concentration. In addition the form of polyelectrolyte molecules is often far from simple and not constant. If the polyelectrolyte is a long-chain molecule such as polymethacrylic acid its form in solution will be a



loose coil, the shape of which is determined by statistics (69). The extension of the coil increases with increasing charge on the molecule as a consequence of growing mutual repulsion between the charged groups. The ionic strength affects the degree of swelling of the coil. A nonlinear polyelectrolyte may be either more like a sponge or network, and also subject to swelling and shrinking, or it may be a more compact and rigid structure as in many native proteins.

Only in the simplest cases are the charge-carrying groups all identical. In most actual cases there are groups of different nature and even of different sign present on one molecule.

No wonder that a theoretical treatment of the relation between charge and pH of polyelectrolytes is a complicated affair and, although a good deal of work has been accomplished, the subject is far from closed.

For a review, papers by Katchalsky [see, for example, (70)] are recommended.

An extremely rapid development in the field began in 1948 when Katchalsky, Künzle, and Kuhn (71), Hermans and Overbeek (72), and Overbeek (73) presented their work in this field at a symposium in Liège (Belgium) and Fuoss and Cathers (74) published a paper on polyvinyl pyridinium compounds. In these early papers the three main aspects of polyelectrolyte theory are clearly recognized. They are: (1) the distribution of the small ions at given charge and configuration of the polyelectrolyte molecule; (2) the relation of charge and configuration with pH and ionic

strength; (3) the interpretation of experimentally accessible magnitudes such as viscosity, sedimentation, light scattering, electrophoresis, etc.

1. Charge and Potential in and around Polyelectrolyte Coils

The distribution of ions around a polyelectrolyte molecule differs from that in the double layers (as described above) insofar that quite often small ions penetrate within the polyelectrolyte molecule and that it surely is not always permissible to consider the charge on the polyelectrolyte molecule as smeared out.

A treatment that may serve as a good basis and allows a number of refinements considers a coiled polyelectrolyte molecule as a rather open spherical structure with a fixed charge smeared out uniformly in a sphere. The distribution of small ions is thought to be governed by the Boltzmann equation, which is valid both inside and outside this sphere. Outside the coil the solutions of the Poisson-Boltzmann equation for spherical symmetry are valid; inside the coil this equation has to be modified as follows to take the fixed charge into account:

$$\operatorname{div} \operatorname{grad} \psi(r) = -\frac{4\pi e}{\epsilon} \sum_i n_i(\infty) z_i \exp\left(-\frac{z_i e \psi(r)}{kT}\right) - \frac{4\pi \rho_0}{\epsilon} \quad (32)$$

in which ρ_0 is the charge density of the fixed charges. The dielectric constant ϵ is assumed to have the same value as in the free solution. The integration constants of the solutions inside and outside the coil have to be chosen in such a way as to avoid discontinuities and infinities, and so that the total charge of the small ions just compensates the fixed charge of one coil. Hermans and Overbeek (72, 75) solved these equations, using the Debye-Hückel approximation. Kimball *et al.* (76) assumed the charge of the coil to be completely compensated within the coil by a constant excess of counterions and a deficit of co-ions just as in a Donnan equilibrium, no double layer being present outside the coil, with a discontinuous transition at the coil boundary. Although this model seems rather crude, it allows the use of the unapproximated Boltzmann equation and it gives a better approximation for the electrical potential within the coil than does the treatment by Hermans and Overbeek. More refined solutions have been obtained by Osawa and co-workers (77), by Fujita (78), and especially by Wall and Berkowitz (63), who solved equation (32) and the corresponding equation (28) by using an electronic computer. Figure 9 gives a comparison of three different solutions for a typical case.

Lifson (79) found an approximated analytical solution which in most cases comes very close to that of Wall and Berkowitz and which may be very useful for further work.

Other distributions than the homogeneous one for the fixed charge ρ_0

have been considered by several of the authors mentioned above. The effect of replacing a homogeneous distribution by a Gaussian one appeared to result in quite minor alterations.

Künzle (80), in order to be able to take the distribution of the charges along the chain better into account, assumed the ionic atmospheres around

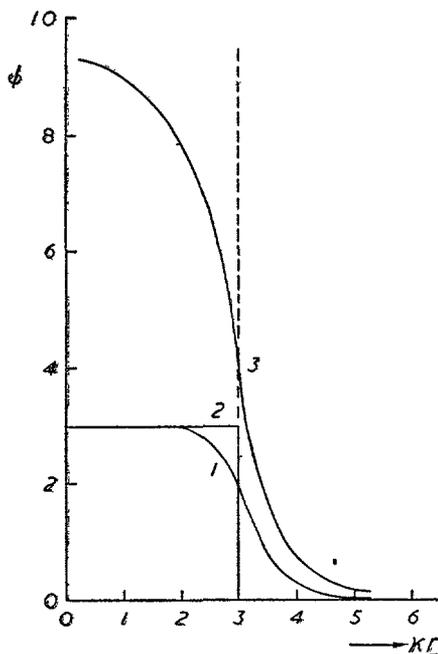


FIG. 9. Radial potential distribution in a polyelectrolyte coil according to: 1. Wall and Berkowitz (63) (exact solution). 2. Kimball *et al.* (76) (Donnan method). 3. Hermans and Overbeek (75) (Debye-Huckel approximation).

the individual charges to be additive. Lifson (79) drew attention to the important interaction effect between neighboring charges. As long as the charge of the coil is rather low the charges will "avoid each other" and the actual interaction will be reasonably well described with a smeared-out distribution. When the charge density, however, is high and neighboring sites on the chain are of necessity charged simultaneously, the nearest neighbor interactions become quite important and have to be added separately to the interaction with more distant charged sites.

2. Titration Curves of Polyelectrolytes

In the absence of interaction between the different charged sites of a polyelectrolyte molecule, the titration curve can be predicted completely

from the dissociation constants of the charged groups. In the simplest case, namely with a single type of charged groups, e.g. COO^- , the titration curve corresponds to that of a monovalent acid.

The interaction among the charged groups and the small ions can be expressed in terms of F_{el} , the electrical part of the free energy of the coil. This quantity can be calculated from the distribution of charge and potential in a straightforward way. In the Debye-Hückel approximation F_{el} is equal to

$$F_{\text{el}} = \frac{1}{2} \int \rho\psi dV \quad (33)$$

where the integration has to include a sufficient volume to include all fixed charges.

The addition of one more elementary charge to the total fixed charge of the coil demands an amount of work, $\frac{dF_{\text{el}}}{dn}$, where n is the number of elementary charges of the coil. This amount of work has to be performed in addition to the normal chemical work of dissociation of the charged groups, and at this stage of dissociation the titration exponent pK is therefore modified as follows

$$K = K_0 \exp\left(-\frac{dF_{\text{el}}/dn}{kT}\right) \quad (34)$$

or

$$pK = pK_0 + \frac{dF_{\text{el}}/dn}{kT} \quad (34a)$$

Overbeek (73) treated this effect using the Debye-Hückel approximation and applying it to the titration curves of gum arabic. From the experimental titration curve F_{el} was determined and from F_{el} the size of the molecule. The radius of the coil was found to be about 100 Å. and to change with charge and ionic strength as predicted. Of course, every refinement used in the description of the double layer can be included in equations (34 and 34a). In the titration curves of proteins these same aspects occur, though in a more complicated way on account of the multitude of types of charged groups. These aspects are treated in the chapter by Linderstrøm-Lang and Nielsen in this volume.

V. ELECTROKINETIC POTENTIALS

So far we have treated charge and potential near the phase boundary but given little attention to their connection with electrophoresis. Charge and potential are equilibrium properties; electrophoresis and electrokinetics in general introduce the aspect of a tangential movement of the two phases along each other. The laws of viscous flow, which govern this

tangential motion, are well known, but there exists great uncertainty about the actual value of the viscosity coefficient, η , in the double layer. The viscosity will be larger than in the free liquid for two reasons: (a) the high field strength; (b) short range interactions between the two phases at the phase boundary.

For solid or highly viscous liquid particles suspended in a liquid it is customary to take these effects roughly into account by assuming the existence of a "slipping plane," parallel to the actual phase boundary, but displaced somewhat to the side of the liquid. The liquid is assumed to be completely immobile between the phase boundary and the slipping plane, but to have its normal viscosity beyond this plane. In accordance with this view electrokinetic phenomena would be determined by the outer part of the electrical double layer and more particularly by the potential at the slipping plane, called the *electrokinetic potential* or ζ -potential.

The electrophoretic velocity, U , is given by the following equation:

$$U = A \frac{\epsilon \zeta}{\eta} E \quad (35)$$

where E denotes the applied field strength; ϵ and η the bulk values of the dielectric constant and viscosity, respectively; and A is a constant, the value of which is given as $\frac{1}{4\pi}$ by Helmholtz (13) and Smoluchowski (81), $\frac{1}{6\pi}$ by Hückel (82), and still other values by Henry (83), Booth (84), Overbeek (85), and others.

Figure 10 shows that the ζ -potential is smaller than the potential ψ_0

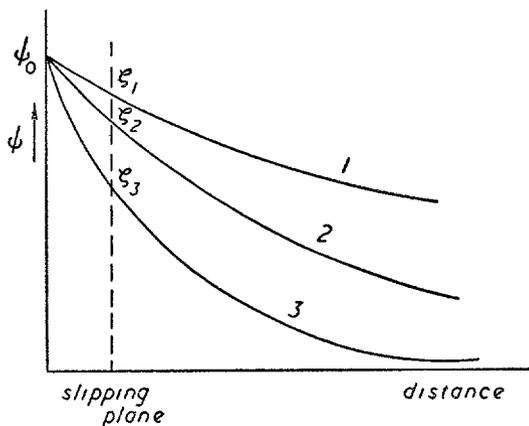


FIG. 10. Curves showing how the potential of the slipping plane decreases with increasing electrolyte content or valence (1 = low, 2 = intermediate, 3 = high ionic strength).

at the phase boundary and that ζ decreases strongly with increasing electrolyte content and valency, even when the surface potential remains constant. Qualitatively this picture is in good agreement with experimental facts. Streaming potentials and electroosmosis in glass capillaries [Freundlich and Rona (86), Rutgers and de Smet (87)] reveal that addition of electrolytes, which affects ψ_0 (or the total potential difference between the two phases) very little, nevertheless causes the ζ -potential to decrease markedly. Still it has not been possible to base a quantitative interpretation of electrokinetics upon this picture. Eversole and Boardman (88), for instance, calculated the distance between the phase boundary and the slipping plane from the electrolyte concentration- ζ -potential relations as found by different authors. In some cases the results can be explained by a constant thickness of the immobile layer, but the thickness varies between 8 and 100 Å. from one series of experiments to another.

Lijklema (26) has suggested recently that the slipping plane might be located at a given field strength in the double layer. Several authors (89-93) have found the viscosity of a liquid to increase in high electric fields. Andrade and Dodd (89) concluded that the increase in viscosity is proportional to the square of the field strength

$$\frac{d\eta}{\eta} = fE^2 \quad (36)$$

where E is the field strength in electrostatic units and f (the "viscoelectric constant") is a constant of the order of 2×10^{-7} in organic solvents. According to this relation the viscosity would increase markedly at fields of 10^6 volts per centimeter. These field strengths can be reached in the double layer. Unfortunately no reliable data exist for water, but it would certainly be worth while to work out this idea in order to relate ζ with ψ_0 .

In the present situation one should be cautious in identifying potentials calculated from electrokinetic data with those derived from adsorption or other thermodynamic measurements.

The situation is least unfavorable when potentials and electrolyte content are low, so that high field strengths do not occur in the double layer.

In the electrophoresis of proteins the first condition is met with often, but the last one is not, and consequently it is uncertain whether one should expect the electrophoretic charge and the adsorption charge or titration charge to be identical.

REFERENCES

1. G. Bakker, in "Handbuch der Experimentalphysik" (W. Wien and F. Harms, eds.), Vol 6, p. 3. Akademische Verlagsges., Leipzig, 1928. See also: *Z. physik. Chem.* A171, 49 (1934).

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10⁻⁶ is not correct

2. E. A. Guggenheim, *J. Phys. Chem.* **33**, 842 (1929); *ibid.* **34**, 1540 (1930).
3. D. A. MacInnes, "The Principles of Electrochemistry," p. 96 ff. Reinhold, New York, 1939.
4. E. Lange and F. O. Koenig, in "Handbuch der Experimentalphysik" (W. Wien and F. Harms, eds.), Vol. 12, Part 2, p. 263-454. Akademische Verlagsges., Leipzig, 1933.
5. P. van Rijsselberghe, *J. Chem. Phys.* **21**, 1550 (1953).
6. K. Möhring, *Z. Elektrochem.* **59**, 102 (1955).
7. E. J. W. Verwey, *Rec. trav. chim.* **61**, 564 (1942).
8. I. I. Tšulyanskii, *Uchenye Zapiski L'vov. Gosudarst. Univ. im. Ivana Franko* **22** (No. 5), 121, (1953); *Referat. Zhur. Fiz.* **1955** (No. 678); *Chem. Abstr.* **50**, 17g (1956).
9. G. Passoth, *Z. physik. Chem. (Leipzig)* **203**, 275 (1954).
10. A. N. Frumkin, Z. A. Iofa, and M. A. Gerovich, *Zhur. Fiz. Khim.* **30**, 1455 (1956), *Chem. Abstr.* **51**, 4173d (1957).
11. N. S. Hush, *Australian J. Sci. Research Ser. A*(1), 480 (1948); *Chem. Abstr.* **44**, 1321e (1950).
12. N. K. Adam, "The Physics and Chemistry of Surfaces," 3rd ed., p. 33. Oxford Univ. Press, London and New York, 1941.
13. H. von Helmholtz, *Physik Wiedemann Ann.* **7**, 337 (1879).
14. J. Perrin, *J. chim. phys.* **2**, 607 (1904).
15. G. Gouy, *J. phys.* (4), **9**, 457 (1910); *Ann. phys.* (9), **7**, 129 (1917).
16. D. L. Chapman, *Phil. Mag.* (6), **25**, 475 (1913).
17. O. Stern, *Z. Elektrochem.* **30**, 508 (1924).
18. D. C. Grahame, *Chem. Revs.* **41**, 441 (1947).
19. R. H. Fowler, *Trans. Faraday Soc.* **23**, 434 (1927).
20. L. Onsager, *Physik. Z.* **23**, 277 (1927); *Chem. Revs.* **13**, 73 (1933).
21. H. A. Kramers, *Proc. Koninkl. Akad. Wetenschap. Amsterdam* **30**, 145 (1927).
22. R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," p. 409. Cambridge Univ. Press, London and New York, 1949.
23. J. G. Kirkwood, *J. Chem. Phys.* **2**, 767 (1934).
24. H. B. G. Casimir, "Tweede Symposium over sterke Electrolyten en de elektrische Dubbellaag," Ed. by Sectie voor Kolloid-chemie, Ned. Chem. Ver. Utrecht, 1944, p. 1.
25. E. L. Mackor, *Rec. trav. chim.* **70**, 763 (1951).
26. J. Lijklema, Thesis, University of Utrecht, 1957.
27. O. Esin and B. Markov, *Acta Physicochim. U.R.S.S.* **10**, 353 (1939).
28. O. Esin and V. Shikov, *Zhur. Fiz. Khim.* **17**, 236 (1943).
29. B. V. Ershler, *Zhur. Fiz. Khim.* **20**, 679 (1946).
30. A. Frumkin, *Izvest. Akad. Nauk SSSR. Otdel. Khim.* **1**, 3 (1940); *Chem. Abstr.* **35**, 3504 (1941).
31. D. C. Grahame, Office of Naval Research; Tech. Rept. No. 13, Jan. 1954.
32. D. C. Grahame, Office of Naval Research, Tech. Rept. 2nd series No. 1, June 1957.
33. J. J. Bikerman, *Phil. Mag.* **33**, 384 (1942).
34. R. Parsons, *Trans. Faraday Soc.* **51**, 1518 (1955).
35. A. L. Loeb, *J. Colloid Sci.* **6**, 75 (1951).
36. W. E. Williams, *Proc. Phys. Soc. (London)* **A66**, 372 (1953).
37. V. Freise, *Z. Elektrochem.* **58**, 822 (1953).
38. B. E. Conway, J. O'M. Bockris, and I. A. Ammar, *Trans. Faraday Soc.* **47**, 756 (1951).
39. J. B. Hasted, D. M. Ritson, C. H. Colle, *J. Chem. Phys.* **16**, 1, 11 (1948).
40. D. C. Grahame, *J. Chem. Phys.* **18**, 903 (1950).

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ital

41. F. Booth, *J. Chem. Phys.* **19**, 1327, 1615 (1951).
42. G. H. Bolt, *J. Colloid Sci.* **10**, 206 (1955).
43. D. C. Grahame, *Chem. Revs.* **41**, 441 (1947); Office of Naval Research, Tech. Rept. Nos. 1 and 3 (1950); *J. Electrochem. Soc.* **98**, 343 (1951); *J. Chem. Phys.* **23**, 1725 (1955).
44. D. C. Grahame, *J. Am. Chem. Soc.* **63**, 1207 (1941); *ibid.* **71**, 2975, (1949); Office of Naval Research, Tech. Rept. No. 2 (1950), No. 6 (1951); *Z. Elektrochem.* **59**, 773 (1955); see also (43).
45. J. Ross McDonald, *J. Chem. Phys.* **22**, 763 (1954).
46. G. and E. Darmais, *Compt. rend.* **238**, 971 (1954).
47. M. A. Vorsina and N. A. Frumkin, *Doklady Akad. Nauk S.S.S.R.* **24**, 918 (1939).
48. A. Watanabe, F. Tsuji, and S. Ueda, *Bull. Inst. Chem. Research Kyoto Univ.* **33**, 91 (1955); *ibid.* **34**, 1 (1956); Proc. 2nd Intern. Congress Surface Activity, London (1957). **3**, 94.
49. J. Th. G. Overbeek and E. L. Maekor, *Compt. rend.* 3me Réunion CITCE, 1951, p. 346. C. Manfredi, Milan, 1952.
50. J. Th. G. Overbeek, *Natl. Bur. Standards (U.S.) Circ.* **524**, 213 (1953).
51. W. L. Freyberger and P. L. de Bruyn, *J. Phys. Chem.* **61**, 586 (1957).
52. I. Iwasaki and P. L. de Bruyn, *J. Phys. Chem.* to be published.
53. D. C. Grahame, *J. Electrochem. Soc.* **98**, 343 (1951); *ibid.* **99**, 273 (1952).
54. E. J. W. Verwey and K. F. Niessen, *Phil. Mag. (7)* **28**, 435 (1939).
55. E. L. Maekor, *Rec. trav. chim.* **70**, 747 (1951).
56. P. Debye and E. Hückel, *Physik. Z.* **25**, 97 (1924).
57. H. Müller, *Kolloidchem. Beih.* **26**, 257 (1928).
58. T. H. Gronwall, V. K. La Mer, and K. Sandved, *Physik. Z.* **29**, 358 (1928).
59. V. K. La Mer, T. H. Gronwall, and L. J. Greiff, *J. Phys. Chem.* **35**, 2245 (1931).
60. G. I. Mikulin, *Ukrain. Khim. Zhur.* **21**, 435 (1955).
61. N. E. Hoskin, *Trans. Faraday Soc.* **49**, 1471 (1953).
62. A. L. Loeb, P. H. Wiersema, and J. Th. G. Overbeek, to be published.
63. F. T. Wall and J. Berkowitz, *J. Chem. Phys.* **26**, 114 (1957).
64. D. Stigter and K. J. Mysels, *J. Phys. Chem.* **59**, 45 (1955).
65. J. Th. G. Overbeek and D. Stigter, *Rec. trav. chim.* **75**, 1263 (1956).
66. G. P. Dube, *Indian J. Phys.* **17**, 189 (1943).
67. M. H. Gorin, in H. A. Abramson, L. S. Moyer, and M. H. Gorin "Electrophoresis of Proteins," p. 126. Reinhold, New York, 1942.
68. R. M. Fuoss, A. Katchalsky, and S. Lifson, *Proc. Natl. Acad. Sci. (U. S.)* **37**, 579 (1951).
69. W. Kuhn, *Kolloid-Z.* **68**, 2 (1934); *ibid.* **76**, 258 (1936).
70. A. Katchalsky, *J. Polymer Sci.* **12**, 159 (1954); *Endeavour* **12**, 90 (1953).
71. A. Katchalsky, O. Künzle, and W. Kuhn, *Helv. Chim. Acta* **31**, 1994 (1948); *Bull. soc. chim. Belges* **57**, 421 (1948).
72. J. J. Hermans and J. Th. G. Overbeek, *Bull. soc. chim. Belges* **57**, 154 (1948).
73. J. Th. G. Overbeek, *Bull. soc. chim. Belges* **57**, 252 (1948).
74. R. M. Fuoss and G. L. Cathers, *J. Polymer Sci.* **2**, 12 (1947).
75. J. J. Hermans and J. Th. G. Overbeek, *Rec. trav. chim.* **67**, 761 (1948).
76. G. E. Kimball, M. Cutler, and H. Samelson, *J. Phys. Chem.* **56**, 57 (1952).
77. F. Osawa, N. Imai, and I. Kagawa, *J. Polymer Sci.* **13**, 93 (1954).
78. H. Fujita, *J. Chem. Phys.* **23**, 837 (1955).
79. S. Lifson, *J. Chem. Phys.* **26**, 700, 727 (1957).
80. O. Künzle, *Rec. trav. chim.* **68**, 699 (1949).

printer! this line should read:
(L. Graetz, ed), Vol. II. p. 366. J. A. Barth, Leipzig 1921

81. M. von Smoluchowski, in "Handbuch der Elektrizität und des Magnetismus"
[(Graetz, ed.) Vol. II. p. 366. Leipzig, 1931.]
82. E. Hückel, *Physik. Z.* **25**, 204 (1924).
83. D. C. Henry, *Proc. Roy. Soc.* **A133**, 106 (1931).
84. F. Booth, *Proc. Roy. Soc.* **A203**, 514 (1950); *Trans. Faraday Soc.* **44**, 955 (1948).
85. J. Th. G. Overbeek, *Kolloid Beih.* **54**, 287 (1943); see also: *Advances in Colloid Sci.* **3**, 97 (1950).
86. H. Freundlich and P. Rona, *Sitzber. preuss. Akad. Wiss. Physik. math. Kl.* **20**, 397 (1920).
87. A. J. Rutgers and M. de Smet, *Trans. Faraday Soc.* **41**, 758 (1945); *ibid.* **43**, 102 (1947); *ibid.* **48**, 635 (1952); *Natl. Bur. Standards (U. S.) Circ. No.* **524**, 263 (1953).
88. W. G. Eversole and W. W. Boardman, *J. Chem. Phys.* **9**, 789 (1941).
89. E. N. Da C. Andrade and C. Dodd, *Proc. Roy. Soc.* **A187**, 296 (1946); *ibid.* **A204**, 449 (1951).
90. J. van Calker and B. Aubke, *Z. Physik* **131**, 443 (1952).
91. A. K. Chernyuk, *Akad. Nauk S.S.S.R. Otdel. Tekh. Nauk Inst. Mashinovedeniya, Soveshchanie Vyazkosti Zhidkostei i Kolloid Rastvorov* **2**, 62 (1944); *Chem. Abstr.* **40**, 3315i (1946).
92. Y. Bjørnstaahl and K. O. Snellman, *Kolloid-Z.* **78**, 258 (1937).
93. I. Osamu Kimura, *J. Chem. Soc. Japan* **64**, 895, 937 (1943).

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