SPACE CHARGE REGIONS IN FIXED CHARGE MEMBRANES AND THE ASSOCIATED PROPERTY OF CAPACITANCE

ALEXANDER MAURO
From The Rockefeller Institute

ABSTRACT The Poisson-Boltzmann equation, which was derived by Shockley in his treatment of the *p-n* semiconductor junction at equilibrium, is applied to fixed charge ionic membranes. The fixed charges in ionic membranes play the same role as "doping" ions in semiconductors, the major difference between the two systems being that in the former the mobile particles are ions while in the latter the particles are electrons and phenomenological particles, "holes." An important consequence of spatial gradients of fixed charge is the presence of space charge regions which give rise to an intrinsic electric field and potential. These quantities are established first for the single "lattice" thus providing a continuous treatment of the Donnan equilibrium invoked by Teorell-Meyer-Sievers in their treatment of fixed charge membranes. It is shown further that when a positive and negative membrane are juxtaposed, the space charge region in the "junction" so formed provides a mechanism for the storage of electrical energy. Thus while the system is basically a "conductor" the presence of transition regions of fixed charge give rise to the additional property of capacitance. Experimental data are presented on ionic and *p-n* junctions. The implications of this mechanism for the physical basis of capacitance in biological cells are discussed.

INTRODUCTION

In order to interpret his data on electrocapillarity, namely, the study of the variation of surface tension at a mercury solution interface with changes in its electrical state, Gouy (1) in 1910 introduced the idea that the combination of thermal motion and electrostatic forces between ions must give rise to an equilibrium distribution in which ions of opposite sign are present at unequal concentrations. To appreciate the novelty of this idea, it should be noted that hitherto the electrical charges at the electrocapillary interface were considered to be present as two single layers of charge of opposite sign, known as the "Helmholtz double layer" in the literature of the related subject, electrokinetics.[1] While Gouy accounted for the ionic distribution

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[1] Electrokinetics is the study of phenomena arising from tangential flow of the bulk electrolyte in the presence of a charged interface as a consequence of applying either a pressure gradient or a potential gradient.

at the interface adequately, a significant contribution to the theoretical analysis was made by Chapman (2) in 1913 when he introduced the Poisson equation of electrostatics to deal with the electrostatic potential associated with the distribution. The terms "diffuse double layer" and "space charge layer" are descriptive of the nature of this distribution of ions and accordingly have been adopted widely in the literature pertaining to this topic.[2]

A very fruitful extension of the Gouy-Chapman analysis was carried out by Debye and Hückel (3) in 1924 for a different situation, namely, a homogeneous solution of strong electrolyte, in an effort to evaluate the energy associated with the electrostatic forces acting between the ions in solution. A facet of their analysis —of immediate importance for our purposes here—was the recognition that the statistical distribution of ionic particles subject to thermal motion and electrical forces could be expressed by the Maxwell-Boltzmann distribution law which hitherto Gouy and Chapman had expressed circuitously by invoking "osmotic forces." Thus with the combined used of Poisson's equation, the so called Poisson-Boltzmann equation became established in the literature of the theory of electrolytes. As a result of the latter work, the analysis of electrocapillary and electrokinetic phenomena has been extended and, in recent years, a further application is seen in the study of the role played by the diffuse double layer in the stability of colloidal suspensions (5) and the properties of monolayers at air-water and oil-water interfaces (6–8).

A new, yet related field in which the Poisson-Boltzmann analysis has played a basic role is the theory of the semiconductor *p-n* junction. The theoretical treatment of this system constitutes the further extension of the space charge analysis to the general case where fixed charges are present and is embodied in the now classic paper of Shockley (9) of 1949. It is our purpose in this paper to indicate that Shockley's analysis, though it was developed for electronic semiconductors, is indeed applicable to ionic systems and in fact constitutes the complete generalization of the Poisson-Boltzmann analysis. This should serve both to emphasize the essentially classical nature of the Shockley analysis in that the particles, electrons and "holes," are subject to the Maxwell-Boltzmann law and Poisson's law as "classical particles," and to elucidate certain similar properties in ionic systems containing fixed charges and mobile ions. The key point to be developed and stressed is that the junctions or transition regions of fixed charge densities of *opposite sign* will give rise to highly localized space charge regions which of necessity confer upon the system the conservative property of *capacitance* in addition to conductance. In the absence of fixed charges, homogeneous electrolytic systems are purely dissipative. The concomitant property, asymmetrical conductance (rectification) though not stressed will be discussed briefly, a more detailed treatment being reserved for a separate communica-

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[2] Stern in 1924 (4) combined the Helmholtz double layer and the Gouy diffuse double layer in his treatment of electrocapillary phenomena.

tion. This subject should be of interest to biophysicists concerned with physical mechanisms associated with physiological membranes, especially since the latter are known to contain fixed charges, *e.g.*, phospholipids and protein, which must inevitably give rise to space charge and capacitive effects.

THEORY

The ionic systems to be considered here—whose importance as a distinct class of electrolytic systems was recognized independently by Meyer and Sievers and by Teorell—[3]are those which contain a homogeneous distribution of immobile ions by virtue of the fact that ionized groups have been attached by chemical means to a "lattice" or meshwork of polymers, *e.g.* polystyrene, polyethylene.

In order to emphasize the essential points and thus avoid distraction with possible higher order effects, it will be assumed at the outset that (*a*) the fixed charges are completely ionized; (*b*) the interstices of the polymer network are permeated by a homogeneous fluid dielectric and mobile ions; (*c*) the polymer network contributes no effect save that it merely serves to immobilize the fixed charges; (*d*) all charges are considered point charges and therefore ionic dimensions are neglected; (*e*) all charges are univalent; (*f*) for simplicity, hydrostatic pressure gradients and volume movements of the fluid as a whole will be considered negligible.

Equilibrium State

Consider the system as depicted in Fig. 1: the fixed charge lattice extends from $x = 0$ to the left, and the electrolytic solution to the right, both of "infinite" extent.

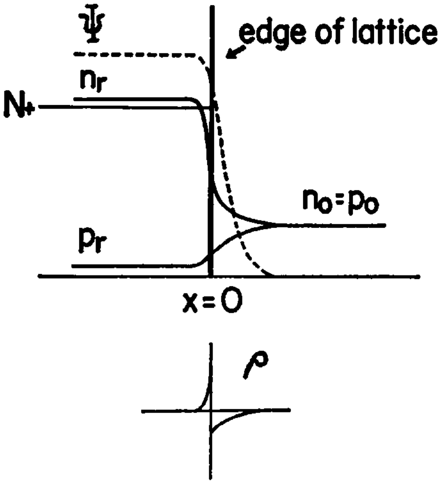

FIGURE 1 Single lattice: Profiles are shown qualitatively for potential and mobile ion concentrations at equilibrium. The lattice containing positive fixed charges extends from $x = 0$ to the left and the electrolytic solution to the right. The space charge ρ is shown below (drawn to smaller scale relative to above).

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[3] A comprehensive treatment of EMF and conductance in single fixed charge membranes can be found in Teorell's review (10).

The fluid dielectric is homogeneous throughout and has a dielectric constant of ϵ. The first fundamental assumption about the physical mechanisms involved is that all mobile species at equilibrium satisfy the Maxwell-Boltzmann distribution and, the second, that the potential energy term is electrostatic, namely $W = \pm q\psi$, q being the charge of the particle and ψ the electrostatic potential. Thus, arbitrarily choosing remote regions to the right in the solution as the zero of the potential, we have

$$n = n_0 e^{-w/kT} = n_0 e^{+q\psi/kT} \tag{1}$$

and

$$p = p_0 e^{-w/kT} = p_0 e^{-q\psi/kT} \tag{2}$$

where n and p refer to the densities (charges per cc) of negatively and positively charged particles, respectively, and n_0 and p_0 the densities at remote regions where the electrostatic potential is zero, k being the Boltzmann constant and T the absolute temperature. The final basic assumption is that the electrostatic potential satisfies Poisson's equation.[4]

Beginning with Poisson's equation, we have that

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi\rho}{\epsilon} \tag{3}$$

It is evident that in general at any point x

$$\rho = (p - n + N_+ - N_-)q \tag{4}$$

where N_+ and N_- are the densities in charges per cc of positive and negative fixed charges, respectively. By means of equation (2) we can express n and p in terms of the potential,

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[4] This aspect of the analysis is the most difficult to justify and therefore warrants some discussion:

A fundamental theoretical difficulty is involved here, namely, in general the potential energy of the particle in the Maxwell-Boltzmann law cannot be obtained from the electrostatic potential derived from Poisson's equation. This procedure is correct in principle only when the potential is small with respect to kT (11–15). In most cases, especially in the space charge regions considered here, $q\psi$ is very large with respect to kT, as much as 30 times, in fact. The potential then should be derived from a more basic consideration, namely, particle-particle Coulomb interaction instead of the Poisson equation. Unfortunately this gives rise to mathematical difficulties that are almost insurmountable. The approximate character of the Poisson equation is, therefore, used as a first order attempt. As pointed out by Booth (16) wherever the Poisson-Boltzmann equation has been employed for $q\psi >> kT$, the theoretical predictions have not been in gross error with respect to experimental observations. Therefore, in spite of the difficulties cited it is used with confidence for the condition $q\psi >> kT$. A lucid discussion of this problem can be found in the text of Rutgers (17).

It is to be noted that Debye and Hückel in their classic treatment did not become involved with these theoretical reservations since they were concerned solely with the integrability of the non-linear Poisson-Boltzmann equation. They noted that the equation assumed a linear and therefore tractable form as a consequence of the fact that sinh $q\psi \approx q\psi$ for $q\psi << kT$—the physical condition of interest to them—and thus working with the linearized equation automatically circumvented the theoretical problem discussed above.

$$\rho = qn_0(e^{-q\psi/kT} - e^{q\psi/kT}) + q(N_+ - N_-) \tag{5}$$

Noting that

$$e^{-a} - e^{a} = -2\sinh a \tag{6}$$

then equation (5) becomes

$$\rho = q(N_+ - N_-) - 2n_0 q \sinh\left(\frac{q\psi}{kT}\right) \tag{7}$$

Thus equation (3) becomes

$$\frac{d^2\psi}{dx^2} = \frac{8\pi n_0 q}{\epsilon}\left[\sinh\left(\frac{q\psi}{kT}\right) - \left(\frac{N_+ - N_-}{2n_0}\right)\right] \tag{8}$$

And expressing ψ in units of kT/q such that

$$y = \psi\Big/\frac{kT}{q} = \frac{q\psi}{kT}$$

we have finally

$$\frac{d^2y}{dx^2} = \frac{8\pi n_0 q^2}{kT\epsilon}\left[\sinh y - \left(\frac{N_+ - N_-}{2n_0}\right)\right]$$

or

$$\frac{d^2y}{dx^2} = \frac{1}{L_D^2}\left[\sinh y - \left(\frac{N_+ - N_-}{2n_0}\right)\right] \tag{9}$$

where

$$L_D = \sqrt{\frac{kT\epsilon}{8\pi n_0 q^2}}$$

L_D is referred to as the "Debye length" of the solution. It is convenient to write equation (9) by expressing distance in units of L_D. Thus, since we have

$$\begin{aligned} \frac{d^2y}{dx^2} &= \frac{1}{L_D^2}\frac{d^2y}{d\xi^2} \\ \frac{d^2y}{d\xi^2} &= \sinh y - \left(\frac{N_+ - N_-}{2n_0}\right) \quad \text{where} \quad \xi = \frac{x}{L_D}. \end{aligned} \tag{10}$$

This is Shockley's basic differential equation for the *p-n* junction at equilibrium.

Note this constitutes the general form of the Poisson-Boltzmann equation in that fixed charges are included. The case considered by Gouy is represented in this equation by the condition of zero fixed charge, wherein a solution of the equation is sought for a given boundary condition of potential at the mercury surface arising from ionic charge due either to adsorption,[5] or to a charging current applied through electrodes connected to the metal and solution,[6] respectively. (In the Debye-Hückel

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[5] Verwey and Overbeek's analysis of the diffuse double layer associated with colloidal particles is most thorough and instructive (5).

[6] In recent years a thorough treatment of the diffuse double layer at the electrocapillary interface is due to Grahame (18).

treatment of this case the equation is linearized since only small values of $q\psi$ are considered.) It is important to note, as will be seen presently, that in the case of finite fixed charge the potential distribution arises *ab initio* from the fact that space charge regions must be present when gradients of fixed charge exist.

(*a*) *Single Lattice.* We shall apply the equation to the ionic system shown in Fig. 1 which we have chosen as the basic configuration of interest. The concentration profile of fixed charge N_+ is a constant extending from $\xi = 0$ to $\xi = -\infty$ and the negative fixed charge N_- is zero throughout.[7] Thus equation (10) becomes

$$2\frac{d^2y}{d\xi^2} = 2\sinh y - \frac{N_+}{n_0}. \tag{11}$$

Rewriting,

$$2\frac{dy}{d\xi}\cdot\frac{d}{d\xi}\left(\frac{dy}{d\xi}\right) = (e^y - e^{-y})\frac{dy}{d\xi} - \frac{N_+}{n_0}\cdot\frac{dy}{d\xi} \tag{12}$$

Integrating,

$$\left(\frac{dy}{d\xi}\right)^2 = e^y + e^{-y} - \frac{N_+}{n_0}\cdot y + c \tag{13}$$

Whereupon,

$$\text{for} \quad \xi < 0 \quad \left(\frac{dy}{d\xi}\right)^2 = 2\cosh y - \frac{N_+}{n_0}\cdot y + c \tag{14}$$

and

$$\text{for} \quad \xi > 0 \quad \left(\frac{dy}{d\xi}\right)^2 = 2\cosh y - 2 \tag{15}$$

$$\text{since for } \xi \rightarrow \infty, \quad \text{both } y \text{ and } \frac{dy}{d\xi} \rightarrow 0.$$

Invoking the boundary conditions:

$$y(0_-) = y(0_+) = y_0 \tag{16}$$

$$\left(\frac{dy}{d\xi}\right)_{0-} = \left(\frac{dy}{d\xi}\right)_{0+}$$

therefore

$$c = \frac{N_+}{n_0}\cdot y_0 - 2 \tag{17}$$

Integrating equations (14) and (15) to obtain the potential, we have

$$\text{for} \quad \xi < 0 \quad -\xi = \int_{y_0}^{y} \frac{dy}{\sqrt{2\cosh y - 2 - \frac{N_+}{n_0}(y - y_0)}} \tag{18}$$

and

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[7] Bartlett and Kromhout (19) have treated a closely related case where a macroion (comparable to N^+ here) is not immobile but is restricted from moving to the right by a thin porous membrane at $x = 0$. This system is usually referred to as the "Donnan equilibrium."

$$\text{for} \quad \xi > 0 \quad \xi = \int_y^{y_0} \frac{dy}{\sqrt{2(\cosh y - 1)}} = \int_y^{y_0} \frac{dy}{2 \sinh \frac{y}{2}} \tag{19}$$

Equation (18) can be evaluated only by numerical (or graphical) integration, noting that y_0 can be established as follows:

Recognizing the boundary conditions, namely,

$$\frac{dy}{d\xi} \quad \text{and} \quad \frac{d^2y}{d\xi^2} \longrightarrow 0 \quad \text{as} \quad \xi \longrightarrow -\infty$$

we have from equation (11),

$$\sinh y_{\infty-} = \frac{N_+}{2n_0} \tag{20}$$

and from equations (14) and (17),

$$y_0 = \left[-2 \cosh y_{\infty-} + \frac{N_+}{n_0} y_{\infty-} + 2 \right] \frac{n_0}{N_+} \tag{21}$$

On the other hand equation (19) can be integrated directly as follows:
let

$$e^{y/2} = \omega$$

then

$$dy = 2 \frac{d\omega}{\omega}$$

and equation (19) becomes

$$2 \int_y^{y_0} \frac{d\omega}{\omega} \cdot \frac{1}{\omega - \frac{1}{\omega}} = 2 \int \frac{d\omega}{\omega^2 - 1} = 2 \int \frac{1}{2} \left(\frac{1}{\omega - 1} - \frac{1}{\omega + 1} \right) d\omega = \ln \frac{\omega - 1}{\omega + 1} \Big]_y^{y_0}$$

and finally

$$\xi = \ln \frac{e^{y_0/2} - 1}{e^{y_0/2} + 1} - \ln \frac{e^{y/2} - 1}{e^{y/2} + 1} \tag{22}$$

(Upon rearranging, equation (22) takes on the form of equation (6) of Verwey and Overbeek (5).) Thus, by means of equations (18) and (19) and the subsidiary relations, equations (20) and (21), the potential y can be evaluated as a function of ξ. Having evaluated y, the concentration of the mobile ions can be obtained by means of equations (1) and (2). The profile of potential and mobile ion concentration thus can be established as a function of ξ as indicated qualitatively in Fig. 1. It is to be noted that Ψ is $y_{\infty-} \cdot kT/q$ as given by (20), *i.e.* the maximum of the electrostatic potential at the remote region in the fixed charge lattice, for a given N_+/n_0.

The behavior of $y(\xi)$ in the solution phase, *i.e.* equation (19), has been investigated by Verwey and Overbeek (5) both by approximate relations and by plotting

$y(\xi)$ for $y_0 = 1, 2, 4$, and 8 in the range $0 \leqq \xi < 3$. The general characteristic of the function is seen as an "exponential" decay from y_0 to zero as $\xi \rightarrow \infty$, the slope $(dy/d\xi)_0$ increasing for increasing values of y_0.

By graphical integration of equation (18) it is seen that $y(\xi)$ in the lattice has a similar character in that the potential rises asymptotically from y_0 to the value $y_{\infty -}$, *i.e.* to its equivalent Ψ as indicated in Fig. 1, the potential drop in the lattice being much smaller than in the solution. (See Appendix for approximate expressions which hold for the condition $N/n_0 >> 1$.)

Donnan equilibrium. It is worthwhile to indicate how the familiar Donnan conditions come out of the general treatment. For remote regions we have from (2) that

$$p_r = p_0 e^{-q\Psi/kT}$$

and

$$\Psi = -\frac{kT}{q} \ln \frac{p_r}{p_0}$$

or

$$n_r = n_0 e^{q\Psi/kT} \tag{23}$$

and

$$\Psi = \frac{kT}{q} \ln \frac{n_r}{n_0}$$

where Ψ is the well known "Donnan Potential." Further, by equating the two equivalent expressions for Ψ we see that

$$\ln \frac{n_r}{n_0} = -\ln \frac{p_r}{p_0} = \ln \frac{p_0}{p_r}$$

or

$$n_r p_r = n_0 p_0 \tag{24}$$

also familiar as the necessary and sufficient condition for the Donnan equilibrium.

It may be of interest to note that conventionally (classical treatment of the Donnan equilibrium) the above relations are derived by considering the ionic concentration c and potential ψ only in the region *remote* from the transition region at $x = 0$ and invoking the condition that for a given species the sum of the electrostatic potential and chemical potential in the region to the left is equal to the sum in the region to the right, namely,[8]

$$\frac{kT}{q} \ln c_r + z\psi_r = \frac{kT}{q} \ln c_0 + z\psi_0 \tag{25}$$

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[8] This method is used by Teorell and Meyer and Sievers to establish the concentrations and potential of the Donnan regions at the membrane-solution interface of fixed charge membranes. The Poisson-Boltzmann analysis constitutes a continuous treatment of such regions.

where c_r becomes n_r and p_r for $z = -1, +1$ respectively, and $\psi_r = \Psi$ and ψ_0 can be chosen as zero. It is to be noted that by invoking the Boltzmann distribution, using the electrostatic potential as the potential energy, just this condition is satisfied. In fact the Boltzmann distribution can be stated as the condition which is satisfied when the sum of the electrostatic and chemical potential is a constant over all values of x, *i.e.* constancy of the "electrochemical" potential throughout the entire region. Perhaps it is useful to point out that the equilibrium condition can also be specified by the condition that the gradient of the electrochemical potential of each of the mobile species vanishes at all points.

(*b*) *Double Lattice.* Having established the profiles for the single lattice we can proceed to consider the consequences of placing a lattice with negative fixed charges at a concentration N_- in the region to the right. To simplify the presentation we shall consider the case in which the concentration N_+ and N_- are equal. In Fig. 2 we can see that the concentration profiles for the mobile ions in both regions are symmetrical except for inversion of the concentration of the positive and negative ions. It should be noted that $x = 0$ is now chosen as the midpoint between the edges of the lattice at $-d$ and d, and the zero of electrostatic potential is arbitrarily fixed for this point. As long as $2d$ is large with respect to L_D, interaction of the diffuse double layers is negligible.[9] However, as $2d$ is made smaller the double layers interact so that the equilibrium conditions are such that the space charge appears less in the solution phase and, in the limit as $2d \rightarrow 0$, resides exclusively in the regions containing fixed charge. This condition is referred to as the abrupt junction in the literature of the *p-n* junction. The corresponding profiles of potential and mobile ion concentration are indicated qualitatively in Fig. 3. As long as N is large with

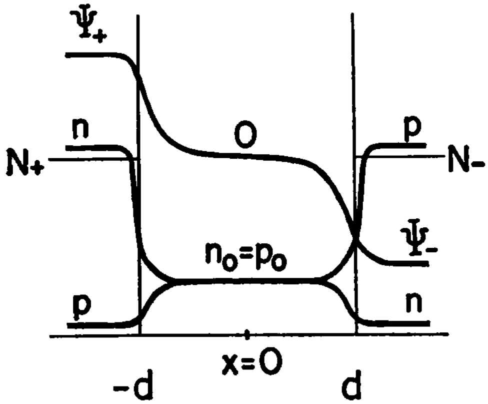

FIGURE 2 Double lattice: Profiles for the case where a lattice containing negative fixed charge groups is separated by a distance $2d$ from one containing positive fixed charges. Note, for convenience the electrostatic potential has been drawn to half scale relative to Fig. 1.

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[9] While it would be desirable to treat the case of the finite distance of separation explicitly the mathematical calculations would be tedious and not warranted for our present purposes, namely, to show how capacitance arises. It will suffice here to deal with the more manageable case, the abrupt junction, in which the capacitive effect is the maximum attainable.

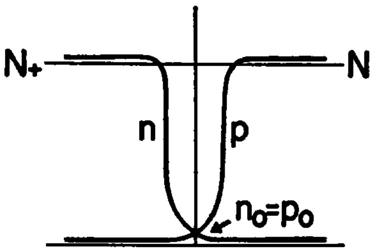

FIGURE 3(a) The profiles of mobile ion concentrations for the abrupt transition. Note the scale for n_0, p_0 has been reduced arbitrarily relative to previous figures to emphasize the assumptions in the "space charge approximation."

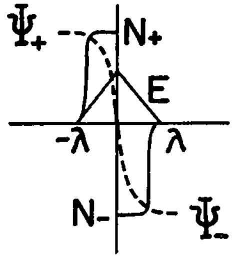

FIGURE 3(b) The corresponding space charge is shown marked by the maximum values, N_+ and N_-. The linear field and parabolic potential are shown also. Note N_+ and N_- are drawn to half scale.

respect to n_0, the fixed charge regions on either side of $x = 0$ and close to this plane are almost completely uncompensated by the mobile ions. (It is to be noted that the scale of p_0, n_0 is greatly exaggerated with respect to N_+ and N_-.) Accordingly, the space charge is *assumed,* to a good approximation,[10] to be due exclusively to the fixed charge profile shown in Fig. 3b where it is indicated that the uncompensated fixed charge density is a constant and drops abruptly to zero at $x = \lambda$, $-\lambda$. (The idealized profiles are seen in Fig. 4.) It may be helpful to note here that the region

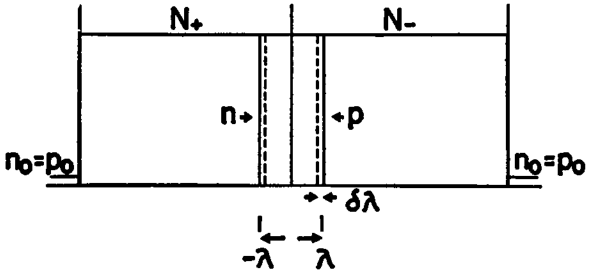

FIGURE 4 The idealized profiles of mobile ion concentration in the transition region for the space charge approximation. The ionic profiles at either solution-lattice interface are not indicated since they are not of interest here.

2λ, as will be seen presently, is quite narrow, *e.g.* $2\lambda << L_D$. The sharply descending profile of either mobile ion and the resulting uncompensated fixed charge region have been verified by computer calculations of equation (10) for the case of a very steep linearly graded fixed charge profile in a study carried out by Morgan and

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[10] In the solid state literature this is known as the "space charge approximation."

Smits (20). Therefore, from heuristic considerations the above approximation is decidedly valid for the step junction which is clearly a limiting case of the linearly graded junction.

The potential and electric field can be obtained by solving the Poisson equation directly, subject to the concentration profile shown in Fig. 3*b*. Thus in the region to the *left* of x = 0, we have, since $E = -(d\psi/dx)$

$$\frac{dE}{dx} = \frac{4\pi q}{\epsilon} N_+$$

Integrating,

$$E = \frac{4\pi q}{\epsilon} N_+ x + B$$

Recognizing the boundary condition, namely, $E = 0$ when $x = -\lambda$, we have

$$B = \frac{4\pi q}{\epsilon} N_+ \lambda$$

Therefore

$$E = \frac{4\pi q N_+}{\epsilon} (x + \lambda) \tag{26}$$

And proceeding in a similar manner for the region to the right of $x = 0$, we have

$$E = -\frac{4\pi q N_-}{\epsilon} (x - \lambda) \tag{27}$$

By integrating again, the potential function can be obtained. Thus in the region to the left from (26) we have, since

$$\frac{d\psi}{dx} = -\frac{4\pi q N_+}{\epsilon} (x + \lambda),$$

that

$$\psi = -\frac{4\pi q N_+}{\epsilon} \left(\frac{x^2}{2} + \lambda x + D\right)$$

Noting that D must be zero since $\psi = 0$ at $x = 0$, thus

$$\psi = -\frac{2\pi q N_+}{\epsilon} [(x^2 + 2\lambda x + \lambda^2) - \lambda^2]$$

or

$$\psi = -\frac{2\pi q N_+}{\epsilon} [(x + \lambda)^2 - \lambda^2] \tag{28}$$

In a similar manner for $x > 0$,

$$\psi = \frac{2\pi q N_-}{\epsilon} [(x - \lambda)^2 - \lambda^2] \tag{29}$$

It can be seen that the potential varies parabolically with x on either side of $x = 0$.

(This profile of potential was predicted by Schottky (21) for the semiconductor region in the metal-semiconductor junction.)

"Pseudo-Equilibrium" State

In order to demonstrate that transition regions of fixed charge give rise to the conservative property, capacitance, it is convenient to assume, as did Shockley, that the conditions are very close to equilibrium ("pseudo-equilibrium") even when a small perturbation δV is superimposed upon the intrinsic potential profile. Thus it follows that the parabolic approximation holds for the perturbed case as for the unperturbed case. We must examine the resulting expansion or contraction of the space charge with applied voltage δV.

If δV is applied such that the right-hand lattice is made incrementally positive and the left-hand negative thus acting to reduce the intrinsic potential difference $\Delta\Psi$, it is seen that charge flows into the junction from either side. Note the edge of the resulting space charge region is indicated by dotted lines in Fig. 4 and its location can be evaluated as follows: From equations (28) and (29) we have,

$$\Delta\Psi = \Psi_{-\lambda} - \Psi_{\lambda} = \frac{4\pi q N}{\epsilon}\lambda^2 \tag{30}$$

where $N = \mathrm{N}_+ = \mathrm{N}_-$
and

$$\Delta\Psi = 2\frac{kT}{q}\ln\frac{N}{n_0} \quad \text{from} \quad (20) \qquad (N \gg n_0).$$

Now if $\Delta\Psi$ is perturbed by an amount δV the space charge will contract, such that

$$\delta V = \delta(\Delta\Psi) = \frac{8\pi q N}{\epsilon}\lambda\,\delta\lambda$$

or

$$\delta\lambda = \frac{\delta(\Delta\Psi)\epsilon}{8\pi q N\lambda} \tag{31}$$

Considering a unit area (cm^2) of junction, the charge flowing in on either side is that contained in the volume $\delta\lambda$, thus

$$\delta Q = qN\,\delta\lambda$$

or from equation (31)

$$\delta Q = \frac{\delta(\Delta\Psi)\epsilon}{8\pi\lambda} \tag{32}$$

But (differential) capacitance C is defined as

$$C = \frac{\delta Q}{\delta(\Delta\Psi)} \tag{33}$$

which from equation (32) becomes

$$C = \frac{\epsilon}{8\pi\lambda} \tag{34}$$

This is an interesting result, namely, the junction behaves as *though* it were a geometrical capacitor with two parallel plates separated at a distance 2λ by a medium of dielectric constant ϵ.

With the aid of equation (30), we have

$$C_{esu} = \sqrt{\frac{\epsilon q N}{16\pi\ \Delta\Psi}} \text{ per cm}^2 \tag{35}$$

Finally, it is convenient to transform to practical units since the capacitance is given here in esu due to the fact that q is expressed in esu. Thus recognizing that

$$1 \text{ coulomb} = 3 \times 10^9 \text{ esu}$$

$$1 \text{ volt} = 1/3 \times 10^{-2} \text{ esu}$$

equation (35) becomes

$$C_{fd} = 1.05\sqrt{\frac{\epsilon q N}{16\pi\ \Delta\Psi}} \tag{36}$$

where from equation (20)

$$\Delta\Psi = \frac{2kT}{q} \ln \frac{N}{n_0} \tag{37}$$

It is pertinent to ask why the single lattice does not display capacitance when perturbed with an applied δV. This is due to the fact that the Poisson-Boltzmann region cannot be perturbed easily but rather the entire voltage δV appears across the lattice as a whole where it appears as an ohmic drop. It is only when two lattices of opposite sign are juxtaposed that the applied δV appears exclusively across the transition zone, *i.e.* superimposes upon the intrinsic electrostatic potential $\Delta\Psi$ thus perturbing the space charge and giving rise to capacitance. That is, in the single lattice electrostatic energy cannot be stored while in the double lattice energy can be stored by virtue of the perturbability of the space charge. Thus the system, while it is basically a conductor, displays also a conservative component.

It is instructive to see what value of capacitance is obtained from equation (36) when the fixed charge density encountered in commercial ionic membranes is used in connection with constants for distilled water.

Assume $N = 0.1$ mole per liter

$= 6 \times 10^{19}$ charges per cc

$\epsilon = 80$

$q = 1.6 \times 10^{-19}$ coulombs

$$n_0 = p_0 = 10^{-7} \text{ moles per liter}$$

$$\Delta\Psi = \frac{2kT}{q} \ln \frac{N}{n_0} \approx 660 \cdot 10^{-3} \text{ volts} \quad \text{at} \quad T = 300° \text{ K}$$

Thus

$$C = 1.53 \ \mu\text{fd per cm}^2$$

Furthermore it is interesting to see the extent of the space charge λ which is obtained from (30):

$$\Delta\Psi = 660 \cdot 10^{-3} \cdot \tfrac{1}{3} \cdot 10^{-3} \text{ esu}$$

$$q = 1.6 \cdot 10^{-19} \cdot 3 \cdot 10^{9} \text{ esu}$$

$$\lambda = \sqrt{\frac{\Delta\Psi\epsilon}{4\pi q N}} = 70 \text{ A}$$

Note L_D is approximately 1 μ or 10,000 A

EXPERIMENTAL RESULTS

The capacitance associated with transition regions of fixed charge has been observed repeatedly in this laboratory. The junctions have been formed by cementing two sheets ("membranes"), one containing positive fixed charges (NH_4^+) and the other negative charges (SO_3^-). The material is available in polystyrene or polyethylene form: Sheets (90 μ thick) of the polystyrene type (Nalfilm[11]) were cemented by placing a thin film of dimethyl formamide on a section (approximately 1 inch × 1 inch) of positively and negatively charged material and allowing to dry for 24 hours under pressure. Sheets of the polyethylene type (AMFion[12]) are thermoplastic and thus were sealed together by means of a Carver press heated to the proper temperature. A two compartment cylindrical lucite cell was used as shown in Fig. 5 to clamp the positive-negative fixed charge junction in place, the cross sectional area being approximately 1.15 cm². One pair of platinum electrodes was arranged to pass current through the junction and one to probe the voltage across it, as shown.

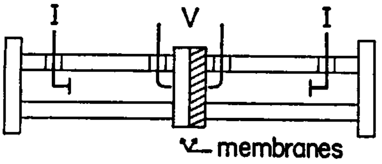

FIGURE 5 The cylindrical lucite cell with the pair of platinum electrodes insulated except for the tips to measure the potential V across the junction. The current electrodes (I) were discs of platinum to provide uniform current density.

It is very important to emphasize again that the nature of the junction is crucial.

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[11] Purchased from National Aluminate Corporation, Chicago.

[12] Kindly supplied by Dr. H. Friedlander of the American Machine and Foundry Company, Springdale, Connecticut.

For example, if the two sheets are merely clamped together, bulging usually occurs with hydration and swelling of the lattice so that the distance of separation d becomes large with respect to L_D and the resulting capacitance is negligible. Although, as was stated in the introduction, the conductance of the junction will not be treated here, it is relevant to point out that if an abrupt transition obtains the resistance of the system is very high—a most remarkable property which has been pointed out by Shockley in his analysis. Thus if a low resistance is observed, this is further evidence for a poor transition region due to a large distance of separation d.[13]

It is well to keep in mind that the responses of interest are those which occur with small magnitudes of current of less than 1 μamp, *i.e.* a voltage drop V of 10 to 15 mv. A typical response resulting from a small applied current with the system in the equilibrium state is seen in Fig. 6*a*. The junction was formed with Nalfilm sheets by the procedure described above. The capacitive behavior is seen clearly and corresponds to approximately 1.0 μfd/cm^2 with a shunt resistance of approximately 60,000 ohms. In Fig. 6*b* the response of the same junction for a small increase in the applied current pulse is shown to demonstrate that the voltage drop becomes asymmetrical at higher voltages, *i.e.*, rectification begins to set in. For comparison a typical response of a *p-n* junction (Tarzian 40-H) for a V of comparable magnitude is seen in Fig. 7. In this case the capacitance at equilibrium is approximately 200 $\mu\mu$fd and the shunt resistance is several megohms. (Note the values are *not* given per square centimeter since the area of the junction could not be measured readily.)

Although the oscillograms have not been included here, it should be noted that junctions in which d is large with respect to L_D give rise to voltage responses that are strictly ohmic; *i.e.*, the voltage response follows the current pulse exactly. It should be emphasized that, in the course of fabricating a series of units, junctions of

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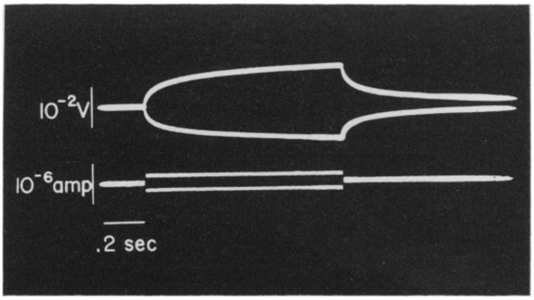
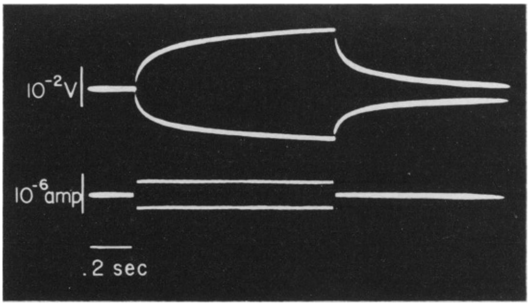
[13] Experiments reported by Gregor (22), Lovrecek *et al.* (23) and Maslov and Ovodova (24) are systems operating in this mode ($2d >> L_D$). In this case the only behavior at low currents is a *pure ohmic drop* across each lattice and the intervening solution. For relatively high current densities rectification is seen due to the fact that the intervening electrolytic phase is being "electrodialyzed"; *i.e.*, ions are being conducted out of the intervening compartment to produce "distilled" water and thus an integral resistance in this layer higher than the initial state; and for a reversal in current the opposite occurs. Since this requires time, the system displays the characteristics of a time-variant resistance of the asymmetrical type as reviewed in a previous paper (25). Note further that the magnitude of resistance observed in this case is much smaller than that which obtains when the unusual transport properties of the junction come into play. For example, a micron layer (1 cm^2) of ordinary distilled water ($.5 \times 10^6$ ohm cm) is approximately 50 ohms whereas the resistance of the junction at equilibrium can be orders of magnitude greater, *e.g.*, in our experiments, 40,000 to 50,000 ohms. (In *p-n* junctions it can be of the order of 0.5 megohms.) The analysis of this effect must be deferred for another communication since this entails considering the difficult problem of the transport of ions across the transition region and new parameters, namely, time of recombination (lifetimes) and diffusion coefficients of the ions, which are not pertinent to the analysis of the space charge capacitance. Furthermore, it also will be seen how in the complete treatment both the real and imaginary components of the admittance are frequency dependent. It will suffice in this communication to deal solely with equilibrium and quasi-equilibrium aspects of the transition region.



6(*a*)



6(*b*)

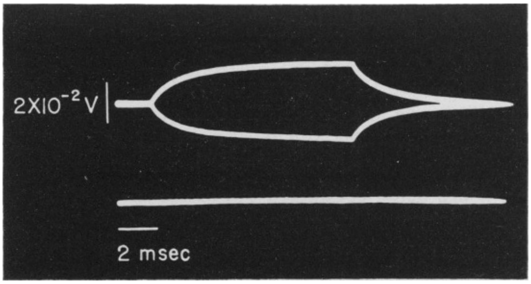


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FIGURE 6(*a*) The response of an ionic junction formed by cementing two nalfilm membranes. The upper tracings indicate the voltage response, the lower the applied constant current step. The double tracings results from applying a forward, and a reverse current.

FIGURE 6(*b*) The same junction at slightly higher current to show asymmetry of voltage response, *i.e.* rectification.

FIGURE 7 Response of a *p-n* junction (Tarzian 40-H). Note time scale used is much shorter than above since capacitance of this system is smaller. The current deflection is not seen here since, the resistance being very high, the applied current was reduced (relative to ionic junctions) to maintain the voltage response close to equilibrium.

this kind are more likely to be encountered than those of the abrupt type. Accordingly, pure ohmic voltage responses are seen more frequently than the typical exponential rise and decay associated with capacitance as indicated above.

The other parameters which determine capacitance, namely, concentration of the electrolyte (n_0, p_0) and fixed charge (N) are being examined experimentally. Furthermore, the interesting property that an applied steady voltage, V, added to $\Delta\Psi$, especially when applied in the reverse direction ("reverse bias"), will give rise to a voltage dependent capacitance—unique with a capacitance of this type and of great importance in solid state technology—is being examined in the ionic junctions. While the relationship $C \propto (V + \Delta\Psi)^{-1/2}$ has not been observed thus far, an inverse relationship of capacitance with bias voltage is seen. These investigations will be reported in a subsequent communication. It will suffice in this paper to present the first order theoretical analysis of the basic capacitive effect and its qualitative experimental confirmation.

DISCUSSION

Physiological Implications. There are many lines of evidence which indicate that the plasma membrane region of the cell contains fixed charges. It will be useful to invoke the familiar bimolecular leaflet of "phospholipids" (*e.g.* see Stoeckenius (26, 27)) as a model of the plasma membrane in order to focus attention on a particular configuration of fixed charge for purposes of discussion. Thus, if it is imagined that the polar end of the lipid molecule consists of positively charged nitrogen attached by a carbon chain to a negatively charged phosphate group, *e.g.* phosphatidyl choline, both on the cytoplasmic and the extracellular border of the leaflet, two transition regions of fixed charge will exist for consideration. Further, it also is assumed that both water and mobile ions are present at some finite concentration in the interstices of the phospholipid lattice, *e.g.* H^+ and OH^-, to specify but a few species. Thus the "plasma membrane" consists of a continuous fluid matrix with two sharp transitions of fixed charge of opposite sign. In either nitrogen-phosphate transition region a space charge must exist subject to the Poisson-Boltzmann mechanism, and therefore, according to the analysis presented here, the property of capacitance must be associated with this system. It should be emphasized that this model is quite different from the one usually invoked by physiologists to explain capacitance in physiological membranes, namely, the plasma membrane is essentially a solid dielectric of close-packed lipids with a dielectric constant of 3 to 5 which separates two conducting media. In the space charge model capacitance is due not to a stratum of dielectric between two conductors but rather to a density gradient of immobile charges of opposite sign within a continuous dielectric matrix throughout which mobile ions are present subject to the Poisson-Boltzmann distribution. That both mechanisms might be operating in a given system such as the cell membrane is, of course, a distinct possibility.

Calculations are being attempted to predict the space charge regions in the bimolecular leaflet. Unfortunately this is more difficult than the analysis presented here based on Shockley's treatment of the *p-n* junction since the fixed charge can no longer be treated as a volume density—rather a surface density must be used along the lines pursued, for example, by Davies in his studies of monolayers containing charged groups (see also Payens (28) and Verwey (29)). Meanwhile the present theoretical and experimental study of the fixed charge system of an extended lattice serves to point out the potential importance and pertinence of the space charge mechanism to physiological membranes and to focus attention on the need for detailed analysis of an explicit system consisting of ionic species in a delimited region comparable to a cell membrane.

Finally, to summarize the overall significance of the study presented here, the Poisson-Boltzmann analysis—in its most general form as given by Shockley—indicates that an electrolytic system need not necessarily be purely dissipative. In fact, if steep transition regions of fixed charges of opposite sign exist, then the system must display in addition to resistance a conservative property, namely, capacitance. In the absence of such regions the resulting homogeneous electrolytic solution displays pure resistance.[14]

APPENDIX

(*a*) Noting that for $N/n_0 >> 1$

$$2 \sinh y \quad \text{and} \quad 2 \cosh y \approx e^{y} \tag{1'}$$

and from (20)

$$e^{y_{\infty-}} \approx \frac{N}{n_0} \tag{2'}$$

equation (21) becomes

$$y_0 \approx \left(-e^{y_{\infty-}} + \frac{N}{n_0} y_{\infty-} + 2\right) \frac{n_0}{N}$$

and

$$y_0 \approx -e^{y_{\infty-}} \cdot e^{-y_{\infty-}} + y_{\infty-} + \frac{2n_0}{N}$$

$$\approx -1 + y_{\infty-} \tag{3'}$$

or

$$y_{\infty-} - y_0 \approx 1$$

This result is interesting since it indicates that the potential drop in the lattice approaches a constant, kT/q volts, for large values of N/n_0.

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[14] It is tacitly assumed here, of course, that energy storage due to the Debye-Falkenhagen effect is strictly negligible, that is, the frequency of the applied field is assumed to be low (very small with respect to the reciprocal of the "relaxation time") and, therefore, the resulting dipole moment of a central ion versus its ionic atmosphere is too small to provide a mechanism for storing electrical energy.

(*b*) Equation (18) can be rewritten as follows:

$$-\xi = \sqrt{\frac{n_0}{N}} \int_{y_0}^{y} \frac{dy}{\sqrt{\frac{n_0}{N}(e^y + e^{-y} - 2) - (y - y_0)}} \tag{4'}$$

For the condition $N/n_0 >> 1$

$$-\xi = \sqrt{\frac{n_0}{N}} \int_{y_0}^{y} \frac{dy}{\sqrt{\frac{n_0}{N}e^y - (y - y_0)}} \tag{5'}$$

Let $y - y_0 = u$, then

$$-\xi = \sqrt{\frac{n_0}{N}} \int_{0}^{y-y_0} \frac{du}{\sqrt{\frac{n_0}{N}e^{y_0+u} - u}} \tag{6'}$$

and from (2′) and (3′)

$$\frac{n_0}{N} \approx e^{-y_{\infty -}} \approx e^{-y_0-1} \tag{7'}$$

thus (6′) becomes

$$-\xi \approx \sqrt{\frac{n_0}{N}} \int_{0}^{y-y_0} \frac{du}{\sqrt{e^{u-1} - u}} \tag{8'}$$

Let $u - 1 = x$ whereupon (8′) becomes

$$-\xi \approx \sqrt{\frac{n_0}{N}} \int_{-1}^{y-y_{\infty -}} \frac{dx}{\sqrt{e^x - x - 1}} \tag{9'}$$

Let $x = -z$, thus

$$-\xi \approx \sqrt{\frac{n_0}{N}} \int_{y_{\infty -}-y}^{1} \frac{dz}{\sqrt{z - 1 + e^{-z}}} \tag{10'}$$

Since $e^{-z} \approx 1 - z + z^2/2$ equation (10′) becomes

$$-\xi \approx \sqrt{\frac{2n_0}{N}} \int_{y_{\infty -}-y}^{1} \frac{dz}{z} \approx -\sqrt{\frac{2n_0}{N}} \ln (y_{\infty -} - y) \tag{11'}$$

Finally,

$$y \approx y_{\infty -} - e^{\xi\sqrt{N/2n_0}} \tag{12'}$$

Thus, equation (12′) establishes that the potential in the lattice rises rapidly indeed from y_0 to the maximum $y_{\infty -}$, the total rise being unity. This behavior is in sharp contrast to the decay of the potential in the solution outside the lattice.

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REFERENCES

1. GOUY, M., Sur la constitution de la charge electrique a la surface d'un electrolyte, *J. Physique,* 1910, **9,** 457.

2. Chapman, D. L., Contribution to the theory of electrocapillarity, *Phil. Mag.* (6) **25**, 475, 1913.
3. Debye, P., and Hückel, E., Zur theorie der elektrolyte. I. Gefrierpunktseiniedrigung und verwandte erscheinungen, *Physik. Z.*, 1923, **24**, 185.
4. Stern, O. Z., *Elektrochem.*, 1924, **30**, 508.
5. Verwey, E. J. W., and Overbeek, J. Th. G., Theory of the stability of lyophobic colloids, New York, Elsevier Publishing Co., chapters II, III, 1948.
6. Davies, J. T., Monolayers of long chain ions, *in* Surface Phenomena in Chemistry and Biology, London, Pergamon Press, Ltd., 55.
7. Palmer, R. C., Effects of salts on soluble ionized monolayers, *in* Surface Chemistry, London, Butterworths., Ltd., 79.
8. Crisp, D. J., Adsorption of amines on negatively charged monolayers, *in* Surface Chemistry, London, Butterworths, Ltd., 65.
9. Shockley, W., The theory of *p-n* junctions in semiconductors and *p-n* junction transistors, *Bell Syst. Techn. J.*, 1949, **28**, 335.
10. Teorell, T., Transport process and electrical phenomena in ionic membranes, *Progr. Biophysics and Biophysic. Chem.*, 1953, **3**, 305.
11. Fowler, R. H., Strong electrolytes in relation to statistical theory, in particular the phase integral of Gibbs, *Tr. Faraday Soc.*, 1927, **23**, 434.
12. Kramers, H. A., *Proc. Acad. Sc. Amsterdam*, 1927, **30**, 145.
13. Onsager, L., *Chem. Rev.*, 1933, **13**, 73.
14. Kirkwood, J. G., On the theory of strong electrolyte solutions, *J. Chem. Physics.*, 1934, **2**, 767.
15. Palmer, R. C., Effects of salts on soluble ionized monolayers, Surface Chemistry, New York, Interscience Publishers, Inc., 1949, 79.
16. Booth, R., The theory of some potential problems in the theory of electrolytes, *J. Chem. Physics*, 1951, **19**, 821.
17. Rutgers, A. J., Physical Chemistry, New York, Interscience Publishers, Inc., 1954, 392.
18. Grahame, D. C., The Electrical double layer and the theory of electrocapillarity, *Chem. Rev.*, 1947, **41**, 441.
19. Bartlett, J. H., and Kromhout, R. A., The Donnan equilibrium, *Bull. Math. Biophysics.*, 1952, **14**, 385.
20. Morgan, S. P., and Smits, F. M., Potential distribution and capacitance of a graded *p-n* junction, *Bell System Techn. J.*, 1960, **39**, 1573.
21. Schottky, W., Vereinfachte und erweiterte Theorie der Randschichtgleichrichter, *Z. Physik.*, 1942, **118**, 539.
22. Gregor, H., personal communication.
23. Lovrecek, B., Despic, A., and Bockris, J. O'M., Electrolytic junctions with rectifying properties, *J. Physic. Chem.*, 1959, **63**, 750.
24. Maslov, V. N., and Ovodova, A. V., Rectification of electric current at ion-exchange membrane boundaries, *Zhur. Fiz. Khim.*, 1960, **34**, 413.
25. Mauro, A., "Anomalous impedance, a phenomenological property of time-variant resistance," *Biophysic. J.*, 1961, **1**, 353.
26. Stoeckenius, W., An electron microscope study of myelin figures, *J. Biophysic. and Biochem. Cytol.*, 1959, **5**, 491.
27. Stoeckenius, W., Schulman, J. H., and Prince, L. M., "The structure of myelin figures and microemulsions as observed with the electron microscope," Kolloid-Zeitschrift, 1960, **169**, 170.
28. Payens, T. A. J., Ionized monolayers, thesis, University of Utrecht, 1955.
29. Verwey, E. J. W., Theory of the electric double layer of stabilized emulsions, *Koninkl. Ned. Akad. Wetenschap. Proc.*, 1950, **53**, 3.