

Discreteness-of-Charge Adsorption Micropotentials

III. Dielectric-Conductive Imaging

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ABSTRACT

A convenient general method for calculating potentials and fields arising from planar arrays of discrete adions under a variety of imaging conditions is described and illustrated. Adions are perfectly imaged by one conducting plane (single imaging) and are also imaged by a dielectric constant discontinuity at a plane on their other side. The method employs only solutions of the single imaging problem, is readily applied without a computer, and is pertinent to the usual electrolyte compact layer adjoining either an electrode or a dielectric material, which may be air. The single image solutions used in calculating more complex imaging results may be exact values obtained from a previous rather complicated approach, or for ease in calculation, may frequently be approximate but quite accurate values calculated by a simple method described herein. Using the exact approach, one can calculate, for the full range of the dielectric reflection parameter, fields and potentials along any line perpendicular to the conducting plane. Here we are primarily concerned with potentials and fields along the line through a removed adion, and the approximate single imaging solution is especially useful. Although we apply the method to regular hexagonal arrays, in the latter case it is equally applicable to arrays described by Grahame's partially smeared, cut-off model for single imaging. Some comparison with the results of this model is presented. In addition to calculating and illustrating the variation of field and potential within the compact layer and the adjoining dielectric medium, we have examined in detail the difference between the micropotential and the macropotential for many different imaging situations. The present study includes the previously treated single conductive plane imaging and also the (infinite) conductive-conductive imaging situations as special cases. It is found that special care is needed to describe the latter situation by the present model. Finally, the effect of possible conductive imaging by the electrolyte diffuse layer is considered qualitatively.

The system we shall consider in this paper is the electrolyte compact double layer (1). We shall assume it consists of a monolayer of ions (effective charge z_0e and average surface charge density q_1) bounded on one side by a plane interface which we shall call the electrode-surface plane (ESP), generally (but not always) associated with an adsorbing conductor, and on the other side by an imaginary plane marking the points of closest approach of the charge centroids of ions in the electrolyte, or diffuse layer. The plane of closest approach is known as the outer Helmholtz plane (OHP), and the plane passing through the charge centroids of the adions in the monolayer is the inner Helmholtz plane (IHP). We shall define γ to be the distance between the OHP and the IHP and β to be the IHP-ESP separation; $d \equiv \beta + \gamma$ is therefore the total thickness of the compact layer.

The situation is illustrated in Fig. 1. The circle centers denote the positions of adion charge centroids. The diagram is not to scale since β is roughly equal to an ionic radius, and the minimum distance between spherical adions in the plane is thus approximately 2β . The present treatment of course applies for adsorption on a curved electrode surface such as a mercury drop provided, as is the case in practice, that the radius of curvature of the surface is much greater than the characteristic microscopic distances involved in the situation such as d and the effective Debye length in the diffuse layer.

The possibility immediately arises that other material besides the ions, such as adsorbed water molecules, may reside in the compact layer; to represent this possibility approximately as well as to take into account to the same degree of approximation the finite polarizability of the adions themselves, we regard these ions as point charges lying on the IHP and take the dielectric constant of the compact layer in which they reside to be ϵ_1 . We have discussed the introduction of such an ϵ_1 in some detail elsewhere (1-4).

The present paper is concerned primarily with the determination of the electrical potential within the compact layer; this is because the potential's behavior is centrally related to virtually every measurable electrochemical property of the system (5). As it turns out, the potential within the system is sensitively dependent on certain structural aspects of the system; not only is it necessary to take the discreteness of the elements into account (6), but correspondingly one may only do so if reasonable models are used for the spatial distribution of the discrete adions within their plane (7). What is "reasonable" depends, it seems, on the temperature, the surface density of the monolayer, the quantities z_0 , β , and γ , and other, more subtle, characteristics of the system. In the present work we shall usually assume that the ions form a perfect hexagonal array with lattice

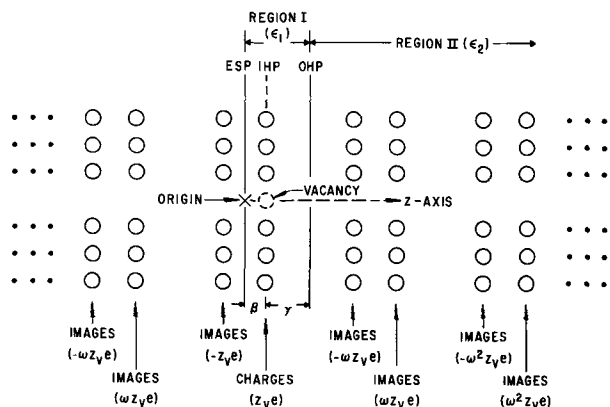


Fig. 1. Cross-sectional diagram of the double layer region showing charges, and some of their images applicable for calculating potential in region I, and the distances β , γ , and z .

constant r_1 , although our general analysis is applicable even without this specific restriction. This is a popular model (3, 4, 7a, 8); and even though it is by no means applicable under all conditions (7), it seems to be a model which is approximately valid for many conditions of interest. As might be suspected, the hexagonal model begins to become inapplicable at low surface densities and/or high temperatures; further discussion of the applicability of this and other models appears elsewhere (7).

There is one other major consideration involved before one can determine the potential in the compact layer: What is the effect of those charges outside the compact layer on the potential? If one of the bounding planes is the surface of a conductor, the effect of those charges on and beyond this plane is straightforward; the conductor acts as an electrical imaging plane, and charges on the conductive surface in excess over those (proportional to q_1) involved in the imaging process set up an additional uniform electric field in the compact layer. If one or both of the bounding surfaces is that of a neutral dielectric insulator, then again a type of imaging is involved. A more difficult question, one which is responsible for much of the variety in the various theories of double layer structure and whose solution has significant impact on the expected properties of such systems, is the effect of the diffuse layer on the potential in the compact layer. One possible approximation is simply to neglect any variation in charge density or polarization within the diffuse layer along directions parallel to the OHP; that is, to assume that these quantities vary only in the direction perpendicular to the OHP. That this is not strictly true is a result of the discreteness-of-charge in the compact layer; that this assumption might still be a good approximation rests on the thermal motion of the ions in the diffuse layer, motion which tends to disrupt any "shadowing" within this layer of the charge density variations on the IHP through pairing of adions with counterions in the diffuse layer. If one makes this approximation, the explicit effect of the diffuse layer goes to naught, and the potential within the compact layer is determined completely by the monolayer ions and the boundary conditions at the other interface. Several more or less correct, exact or approximate, treatments of this model have appeared in print (4, 8c-f, 9, 10). The above situation, with a metal electrode, has been termed by the present authors the "single-imaging" case in a treatment (4) hereafter referred to as II.

At the extreme opposite end of things, another model of the diffuse layer's effect has been proposed and treated (3, 7b, 8b-f, 11). This might be termed the "Ershler model" after its first proponent; the present authors have dealt with this model in some detail and have termed it the "infinite-imaging" case in a treatment (3) hereafter referred to as I. As the latter terminology implies to some of us, this model assumes that mobile diffuse-layer ions are capable of arranging themselves so as to make the OHP an equipotential surface. Effectively then, the OHP becomes a second conductive-imaging plane (exactly as though it were a metal surface) and the outcome of this is an infinite set of images, as in a hall of mirrors.

Unfortunately it has not been possible to establish unequivocally, either experimentally or theoretically, which of these two models more nearly represents the actual behavior of the diffuse-layer ions. An adequate treatment of the diffuse layer in the vicinity of the OHP, where the influence of the discrete compact-layer ions is greatest and the usual approximations most hazardous, may be as yet an unfinished assignment. The most promising approaches have been those of Stillinger and Kirkwood (12) and some of the Russian workers (13); however, even these treatments invoke expansions involving the ratio of electrical energy to thermal energy in the diffuse layer, and for concentrations of interest the validity of such

theories is uncertain. The experimental problems are almost as sticky: The quantities actually measured are only related to local potentials after an "interpretive process" which is somewhat questionable; for example, isothermal measurements leading to adsorption coverages (q_1) only yield adsorption potentials vs. coverage if the form of the isotherm is known. Furthermore, it is possible that the state of ionization of the monolayer elements may change over certain ranges of surface coverages for some systems (2, 14, 15).

Returning to the refuge of our idealized situation, however, there is one diffuse-layer effect which should exist independent of the behavior of the diffuse-layer ions: In most situations there is a fairly abrupt change in the dielectric constant in going across the OHP. If we denote the dielectric constant of the bulk electrolyte, containing no excess ions, by ϵ_2 , the difference $\epsilon_2 - \epsilon_1$ will induce dielectric imaging at the OHP. [We should note that the major dielectric constant change may not occur precisely at the OHP, so that the imaging plane may lie somewhat within the compact layer (16). This possibility will be neglected here.] When this imaging is accompanied by metallic imaging at the ESP, resulting in an infinite set of imperfect images, as though in a hall of imperfect mirrors, we have described this dielectric-conductive situation as the "partial-imaging" case. This case has the following features of particular interest. First, this type of imaging should be present in most systems, whatever additional effect may be present due to the diffuse-layer ions. The dielectric discontinuity, or an approximation thereto, would be expected in most cases, forming a "background effect" for any additional action by the diffuse-layer ions. In view of this effect, it is in fact difficult to construct an electrolytic system which displays "single imaging," and we now regard this case to be of interest only in reference to nonelectrolyte systems or as a least-imaging limiting case for electrolytes.

Since we plan to compare many of the theoretical single, partial, and infinite imaging discreteness-of-charge treatments mentioned above in a forthcoming review (17), we shall omit much of such cross-comparison from the present paper. It is perhaps worth mentioning that the present work contains in a certain sense all the results of the limiting cases I and II and also yields a continuous bridge between them. Although the present paper does not include a treatment of dielectric-dielectric imaging, a case treated to some extent by Levine *et al.* (7b), our present, easily applied methods require, as we shall show elsewhere, only simple modifications to apply to this situation as well.

General Analysis

In the remainder of this paper we shall be primarily concerned with the potential which results when a single vacancy is present in an otherwise perfect hexagonal array of adsorbed ions. As has been discussed in I and II, this leads to the interesting part of the micropotential; the effects of omitted self-images are independent of q and q_1 and may be subsumed into the "chemical" part of the adsorption potential. The potential ψ in our present work consists of two contributions: a discrete-charge contribution ψ_a which is always present whatever the charge on the ESP and a uniform-displacement component ψ_e which results from an additive constant D field normal to the ESP and vanishing when the ESP is grounded so its charge q becomes equal to $-q_1$ for dielectric-conductive imaging. We first determine the discrete-charge contribution ψ_a . The basic method is to replace the ESP and OHP interfaces with a system of fictitious "image charges," the particular system depends on whether we seek the potential on the metal side or the solution side of the OHP. Thus, referring to Fig. 1, the potential between the metal and the OHP (region I) will derive from an infinite

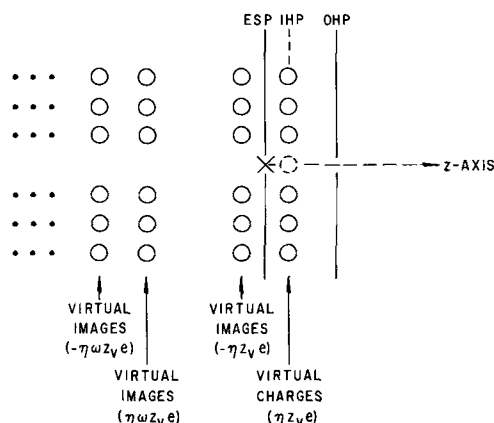


Fig. 2. Cross-sectional diagram of the double layer region showing effective charges and some of their virtual images applicable for calculating potential in region II.

set of images (for each charge on the IHP) as though the whole space were of dielectric constant ϵ_1 ; referring to Fig. 2, the potential on the solution side of the OHP (region II) will likewise involve an infinite set of images, and the whole space of region II is to be regarded as having dielectric constant ϵ_2 . The sets of images for each charge on the IHP are chosen so that the resulting potentials satisfy the appropriate conditions on the ESP and OHP. In particular, the resulting potential should be zero on the ESP, continuous across the OHP, and result in a continuous variation in the normal component of electric displacement across the OHP. It may be verified by inspection that the set of images indicated in Fig. 1 and 2 lead to potentials satisfying these conditions.

We shall set up a coordinate system as follows: The positive z -axis is taken normal to the ESP, extending outwards towards the OHP. The x and y axes lie in the ESP, and the origin of coordinates is on the ESP and the normal line passing through the vacancy. Although the methods of the present paper may be readily extended to give potentials for positions other than $x = y = 0$, in the following we shall only be concerned with actually calculating the potential (and field) along this line.

Let us now define $\omega \equiv (\epsilon_2 - \epsilon_1)/(\epsilon_2 + \epsilon_1)$, and $\eta \equiv 1 + \omega = 2\epsilon_2/(\epsilon_1 + \epsilon_2)$. Referring to Fig. 1, we see that the array of adions and their images giving rise to ψ_a in region I form sheets of nonideal dipoles whose centers lie on the planes $z = z_n \equiv 2nd$ where n is an integer. The separation between the positive and negative charge of each nonideal dipole is 2β , and the strength of the dipole sheets drops off as $\omega^{|n|}$. Similarly, referring to Fig. 2, it may be seen that the potential ψ_a in region II derives from a set of nonideal dipoles similar to those pertaining to region I. The differences between the sets for the two regions are that the positive- n sheets are missing for the region II calculation and the dipole strengths are all multiplied by the factor η .

If we now define $\psi_{ao}(x, y, z)$ to be the potential produced at (x, y, z) by our array of adions in the single-image regime (the quantity known as ψ_a in II) we may take the foregoing into account and write $\psi_a(x, y, z) = \psi_{ao}(x, y, z)$

$$+ \sum_{n=1}^{\infty} \omega^n \{ \psi_{ao}(x, y, z + 2nd) - \psi_{ao}(x, y, 2nd - z) \} \quad [1]$$

in region I, and in region II

$$\psi_a(x, y, z) = (\eta\epsilon_1/\epsilon_2) \sum_{n=0}^{\infty} \omega^n \psi_{ao}(x, y, z + 2nd) \quad [2]$$

where $\eta\epsilon_1/\epsilon_2 = 1 - \omega$. Thus, we have expressed the partial-image potential in terms of a single series (instead of the double or triple series used by others) involving the accurately known (4) single-image potentials. Levine *et al.* (7b, 11) have employed a similar approach (for the infinite imaging case), in which they used Grahame's cut-off model (8c) for the single image potential $\psi_{ao}(0, 0, z)$. Similarly, defining $\mathcal{E}_a$ as the electric field associated with ψ_a in the present regime and $\mathcal{E}_{ao}$ as the field associated with the single-imaging potential ψ_{ao} , one obtains in regions I and II, respectively

$$\mathcal{E}_a(x, y, z) = \mathcal{E}_{ao}(x, y, z)$$

$$+ \sum_{n=1}^{\infty} \omega^n \{ \mathcal{E}_{ao}(x, y, z + 2nd) + \mathcal{E}_{ao}(x, y, 2nd - z) \} \quad [3]$$

$$\mathcal{E}_a(x, y, z) = (\eta\epsilon_1/\epsilon_2) \sum_{n=0}^{\infty} \omega^n \mathcal{E}_{ao}(x, y, z + 2nd) \quad [4]$$

These single-summation expressions for ψ_a and $\mathcal{E}_a$ converge quite rapidly; even for $\omega = 1$, the expression for potential in region I converges well. As ω approaches unity, the value of ψ_a in region II is bounded

$$\psi_a \leq (\eta\epsilon_1/\epsilon_2) \sum_{n=0}^{\infty} \omega^n \psi_{ao} = \eta\epsilon_1\psi_{ao}/\epsilon_2(1 - \omega) = \psi_{ao}$$

where the upper bound, ψ_{ao} , is defined as in II; thus $\psi_{ao} \equiv 4\pi\beta q_1/\epsilon_1$. In carrying out the sums for $\psi_a(0, 0, z) \equiv \psi_a(z)$ it was usually found to be more convenient to use an approximate but highly accurate analytic expression for $\psi_{ao}(0, 0, z) \equiv \psi_{ao}(z)$ than to use the exact results obtainable from II. The approximation used and its accuracy is discussed further in ref. (18) and in the Appendix. Calculation of $\psi_{ao}(z)$ by this approximation is far simpler than by the lengthy expressions given in II, yet yields adequate accuracy. The accuracy of the results in the present paper have, in fact, been checked by calculating many of them with both exact and approximate values for $\psi_{ao}(z)$.

To complete the potential, we must add the uniform D field part, ψ_e . The boundary conditions at the ESP require that, if the total surface charge density on the ESP is q , then the uniform field produced is simply $4\pi(q + q_1)$. Taking the zero of ψ_e to lie on the ESP, we obtain $\psi_e = -(4\pi/\epsilon_1)(q + q_1)z$ for region I and $\psi_e = -4\pi(q + q_1)[(d/\epsilon_1) + \{(z - d)/\epsilon_2\}]$ for region II. We note, incidentally, that if ψ_{aic} and $\mathcal{E}_{aic}$ (see II) are substituted for ψ_{ao} and $\mathcal{E}_{ao}$ in the foregoing equations, the resulting potentials and fields are the ones pertaining to a complete adion array.

Before presenting detailed results of our calculation of potentials, fields, and other quantities of interest, we point out an interesting feature pertaining to the limit $\omega \rightarrow 1$. Intuitively one might expect ψ_a (in region I) to approach the infinite-image (conductive-conductive) ψ_a as ω approaches unity. As it turns out, however, this preconceived notion is entirely wrong: The limiting behavior of the present ψ_a is distinctly different from the ψ_a determined in I, which we shall here denote as ψ_{acc} . Thus one cannot simply take $\omega = 1$ herein and directly obtain ψ_{acc} . What does occur for given q and q_1 is that the limiting value of the present $\psi_a = \psi_a + \psi_e$ is identical to the value of $\psi_{acc} + \psi_e$ obtained by redefining ψ_e (in I) so as to place its zero on the ESP (as has been done with our present partial-imaging ψ_e). In other words, the actual limiting behavior of the present ψ_a is given by $\lim_{\omega \rightarrow 1} \psi_a = \psi_{acc} + (4\pi q_1 z \beta / \epsilon_1 d)$. In particular, at the OHP where ψ_{acc} is zero, $\lim_{\omega \rightarrow 1} \psi_a = \psi_{ao}$. This behavior represents a real physical effect and not just a trivial definition of the zero of potential. The physical origin of the effect lies in the fundamental difference between

a dielectric, no matter how "strong," and a conductor. Only the conductor allows charge to build up on its surface so as to render the field inside exactly zero.

Normalized Equations

For presentation and comparison purposes, it is convenient to deal with normalized equations whenever practical. We shall normalize potentials with the ψ_∞ introduced above and shall denote such quantities as ψ_{ao}/ψ_∞ and ψ_a/ψ_∞ as ψ_{ao}^N and ψ_a^N , respectively. Note that since ϵ_1 occurs in ψ_∞ , a potential such as ψ in region II, where $\epsilon = \epsilon_2$, is still normalized by a quantity involving ϵ_1 , not ϵ_2 , in this convention. It will prove convenient to normalize fields in an equivalent way, using $\mathcal{E}_\infty \equiv -4\pi q_1/\epsilon_1$. Finally, we will normalize electric displacements with $\mathcal{D}_\infty \equiv -4\pi q_1$.

From now on let us take $x = y = 0$ and define $Z \equiv z/\beta$ and $R_1 \equiv r_1/\beta$. Further, let $\gamma/\beta \equiv \Gamma$, $Z_0 \equiv 1 + \Gamma \equiv d/\beta$, and $\rho \equiv 2Z_0$. Then the IHP occurs at $Z = 1$ and the OHP at $Z = Z_0$. For some purposes, as we shall see, it is useful also to use the normalized variable $\xi \equiv Z/R_1 \equiv z/r_1$.

We may now omit reference to x and y and write in place of [1] and [2]

$$\psi_a^N \equiv \psi_a^N(Z; R_1) = \psi_{ao}^N(Z; R_1) + \sum_{n=1}^{\infty} \omega^n \{ \psi_{ao}^N(n\rho + Z; R_1) - \psi_{ao}^N(n\rho - Z; R_1) \} \quad (5)$$

(region I, $0 \leq Z \leq Z_0$)

$$\psi_a^N \equiv (1 - \omega) \sum_{n=0}^{\infty} \omega^n \psi_{ao}^N(n\rho + Z; R_1) \quad (6)$$

(region II, $Z \geq Z_0$).

Equations following from [3] and [4] may be similarly written; instead, since it proves more convenient to plot displacements than fields, we give equations for $\mathcal{D}_a^N \equiv \mathcal{D}_a/\mathcal{D}_\infty$, equal to $\epsilon_1 \mathcal{E}_a/\epsilon_1 \mathcal{E}_\infty$ in region I and to $\epsilon_2 \mathcal{E}_a/\epsilon_1 \mathcal{E}_\infty$ in region II. To obtain $\mathcal{E}_a^N$ in region II, we need only multiply $\mathcal{D}_a^N$ in this region by $(\epsilon_1/\epsilon_2) = (1 - \omega)/(1 + \omega)$. The results for $\mathcal{D}_a^N$ are

$$\mathcal{D}_a^N = \mathcal{E}_{ao}^N(Z; R_1) + \sum_{n=1}^{\infty} \omega^n \{ \mathcal{E}_{ao}^N(n\rho + Z; R_1) + \mathcal{E}_{ao}^N(n\rho - Z; R_1) \} \quad (7)$$

(region I)

$$\mathcal{D}_a^N = (1 + \omega) \sum_{n=0}^{\infty} \omega^n \mathcal{E}_{ao}^N(n\rho + Z; R_1) \quad (8)$$

(region II)

For use in comparing with experimental results, it is frequently useful to have available complete potentials and fields which include the uniform D field contributions. We may write

$$\psi^N = \psi_a^N + \psi_e^N \quad (9)$$

$$\mathcal{E}^N = \mathcal{E}_a^N + \mathcal{E}_e^N \quad (10)$$

where $\epsilon_a^N = \mathcal{D}_a^N$ and $\{(1 - \omega)/(1 + \omega)\} \mathcal{D}_a^N$ in regions I and II, respectively, and

$$\psi_e^N = -\{1 + (q/q_1)\}Z \quad (11)$$

$$\mathcal{E}_e^N = -\{1 + (q/q_1)\} \quad (12)$$

$$\psi_e^N = -\{1 + (q/q_1)\}[Z_0 + \{(1 - \omega)/(1 + \omega)\}(Z - Z_0)] \quad (13)$$

$$\mathcal{E}_e^N = -\{1 + (q/q_1)\}[(1 - \omega)/(1 + \omega)] \quad (14)$$

There is, of course, no average D field contribution when $q = -q_1$ and the ESP is grounded.

The micropotential ψ_1 is related to the energy required to move an ion at the OHP to its adsorbed position at the IHP. This definition does not include the small p. d. V_2 in the diffuse layer between the

OHP and the bulk of the solution. It is actually $\psi_1 + V_2$ which appears in an adsorption isotherm, but we shall neglect V_2 hereafter since it depends on q and q_1 and can be added in whenever pertinent. Remark, however, that unless the OHP is taken as an equipotential surface, which implies conductive imaging there, the usual one dimensional diffuse-layer theory is inconsistent with the requirement that the potential be continuous across the OHP. On the other hand, even when the OHP is not an equipotential, the value of V_2 , now a function of x and y , will probably be quite close to that predicted by the usual one-dimensional theory.

From the above discussion, we have $\psi_1 \equiv \psi(\beta) - \psi(d)$. We wish to compare this p. d. to the average p. d., V_1 , across the inner region. The average potential itself, $V(z)$, may be written in normalized form as (3)

$$V^N(Z) = -[Z(q/q_1) + (Z - 1)] \quad (15)$$

for $Z \geq 1$. It is taken zero at $Z = 0$. V_1^N is then $-V^N(Z_0)$. It will be convenient to introduce the normalized quantity $\lambda \equiv \gamma/d = \Gamma/(1 + \Gamma) = \Gamma Z_0^{-1}$. For ψ_1^N we readily obtain

$$\psi_1^N = \psi_a^N(1) - \psi_a^N(Z_0) + \Gamma\{1 + (q/q_1)\} \quad (16)$$

As in II, let us form the ratio (applicable for $Z_0 \geq 1$)

$$\Delta \equiv \psi_1/V_1 = -\psi_1^N/V^N(Z_0) \equiv \lambda(1 + \Delta) = \frac{\Gamma\{1 + (q/q_1)\} + \Delta\psi_a^N}{\Gamma + (1 + \Gamma)(q/q_1)} \quad (17)$$

where Δ is defined in [17] and $\Delta\psi_a^N \equiv \psi_a^N(1) - \psi_a^N(Z_0)$. The quantity Δ , which measures the deviation from linear proportionality of the micropotential to V_1 , follows from [17] and may be written

$$\Delta = \frac{1 + \lambda^{-1}\Delta\psi_a^N}{\Gamma + (1 + \Gamma)(q/q_1)} \quad (18)$$

When $q = 0$, we define $\Delta \equiv \Delta_0$, where

$$\Delta_0 = \Gamma^{-1}[1 + \lambda^{-1}\Delta\psi_a^N] \quad (19)$$

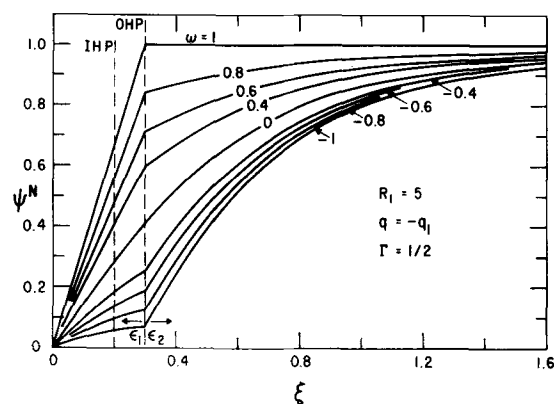
Discussion of Results

Conducting ESP

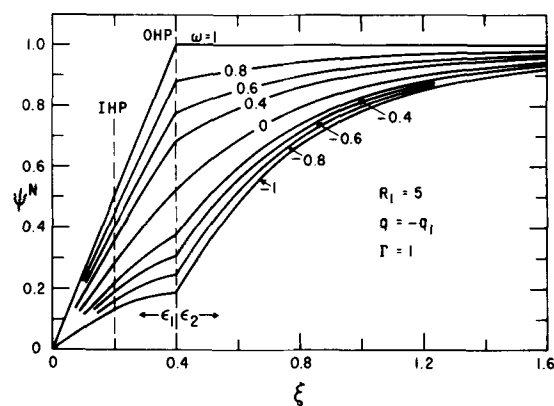
In this section, we shall consider the usual electrolyte situation shown in Fig. 1 of a conducting electrode, a compact inner layer, and a diffuse layer extending beyond the OHP. We shall, for the time being, ignore effects arising from moveable ions in the diffuse layer and shall only be concerned with the effect of the $\epsilon_1 - \epsilon_2$ dielectric discontinuity at the OHP.

Suggested values of ϵ_1 in the compact layer have ranged from 6 to about 15 [see ref (1)]. The value of ϵ_2 for an aqueous electrolyte can be no greater than 81 at room temperature and will likely be appreciably reduced in the diffuse layer because of dielectric saturation arising from the average field there and the effects of closely neighboring ions (1, 19, 20). A reasonable approximate lower value for ϵ_2 might therefore be 50. Those combinations of the above values of ϵ_1 and ϵ_2 which give the smallest and largest ω 's lead to $\omega_{\min} \sim 0.54$ and $\omega_{\max} \sim 0.86$. The smaller is ω , the less is dielectric imaging alone likely to approximate well to the actual electrolyte situation including diffuse layer conductive imaging. In the succeeding figures, however, we have shown results for a variety of values of ω between $+1$ and -1 , for completeness, for comparison with the results of I and II, and because some of the negative values are pertinent to the situation discussed in the next section.

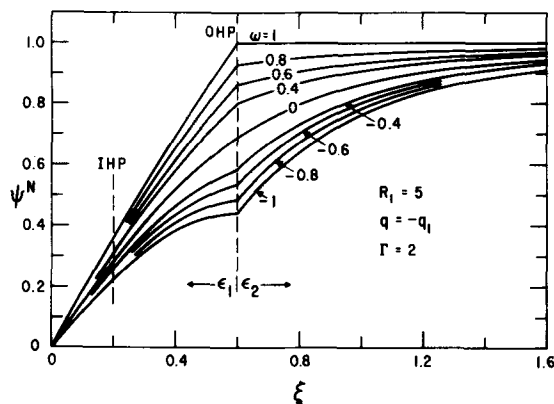
Figures 3 and 4 show the dependence of normalized potential and displacement on normalized distance from the ESP, ξ , for a number of ω values for the choice $R_1 = 5$ and several values of Γ . These values of Γ probably cover the experimentally likely possibilities for such electrolytes as KI. We have used



(a)



(b)

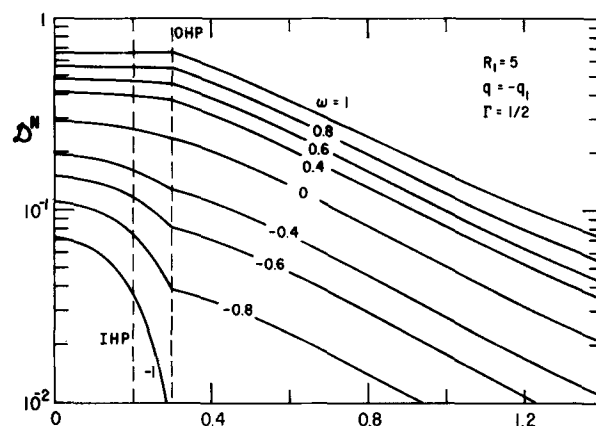


(c)

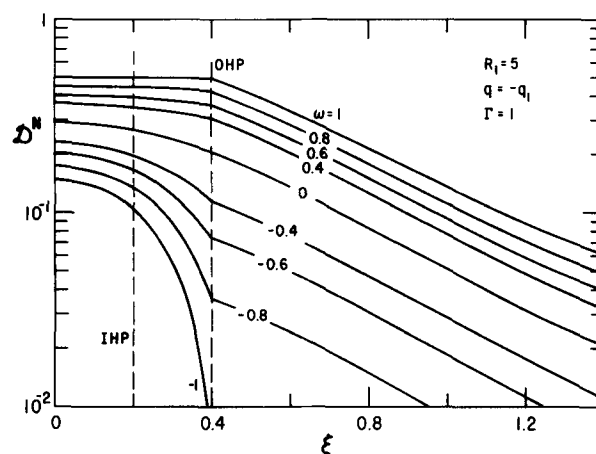
Fig. 3. Normalized discrete potential $\psi^N = \psi_a^N$ vs. normalized distance from ESP, $\xi \equiv Z/R_1$, for $R_1 = 5$ and $\Gamma \equiv \gamma/\beta$ equal to $1/2$, 1 , and 2 . The parameter is $\omega \equiv (\epsilon_2 - \epsilon_1)/(\epsilon_2 + \epsilon_1)$.

the parameter ξ here instead of Z itself because we have found elsewhere (4, 18) that for single imaging ($\omega = 0$) $\psi_a^N = \psi_{ao}^N$ is a function primarily of ξ and depends only slightly on R_1 separately. The present curves may thus be compared directly with others plotted vs. ξ . Unfortunately, when $\omega \neq 0$, such virtual independence of R_1 is less marked, as we shall demonstrate elsewhere.

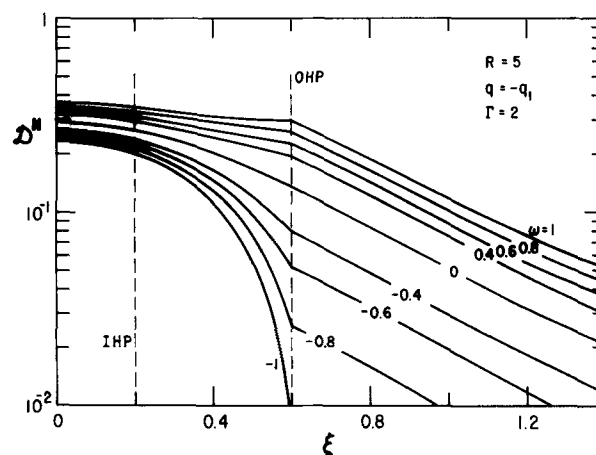
For greatest clarity and distinction between curves, we have taken $q = -q_1$ in Fig. 3 and 4. This choice has the effect of making $\psi^N = \psi_a^N$ and $\mathcal{D}^N = \mathcal{D}_a^N$. Although q seldom equals $-q_1$ in electrolyte situations, ψ^N and $\mathcal{D}^N$ for $q \neq -q_1$ may be readily derived from the curves given through the use of Eq. [9] and [10], [11], and [12], and the known relations between $\mathcal{E}^N$ and $\mathcal{D}^N$. We have elected to plot $\mathcal{D}^N$ in Fig. 4 rather



(a)



(b)



(c)

Fig. 4. Normalized discrete displacement $\mathcal{E}^N = \mathcal{E}_a^N$ vs. ξ for $R_1 = 5$, $\Gamma = 1/2$, 1 , 2 , and a variety of ω values.

than $\mathcal{E}^N$ to avoid the discontinuities which would otherwise appear at the OHP. It is interesting to note that discontinuities still appear in the first derivative of $\mathcal{D}^N$ except when $\omega = 0$. Because of the infinite discontinuities which occur in some quantities at $\omega = 1$ and -1 , our present results do not serve to yield $\mathcal{E}_a^N$ for $Z_o \geq 1$ when $\omega = -1$, but they do show that $\mathcal{E}_a^N = 0$ for $Z_o \geq 1$ when $\omega = 1$. The missing $\mathcal{E}_a^N$ portion for $\omega = -1$ can be readily calculated directly from Eq. [8], however, by first multiplying it by $(1 - \omega)/(1 + \omega)$ and then letting $\omega = -1$.

Although the present method of calculating ψ^N and $\mathcal{D}^N$ for any pertinent values of ω , Z , and R_1 is suffi-

ciently simple that no computer need be used to achieve 1% or better accuracy, we have required for this paper so many values of these and other related quantities that we have, in fact, used a computer for their calculation. We have made a careful comparison between the results of the approximate formulas for ψ_{ao}^N and $\mathcal{E}_{ao}^N$ given in the Appendix and very accurate values of these quantities calculated as in II. This comparison shows, for example, that $R_1 = 5$ the use of the (3/3) approximant for $p(\xi)$ given as (a) in Table I of the Appendix yields values of ψ_a^N for any reasonable Z , Γ , and ω choices which generally differ from the accurate ones by only a small amount in the fifth significant figure. The results for ψ_a^N are thus at least as accurate as those for $p(\xi)$ itself and are usually more accurate. This approximant, or an even simpler one given in ref. (18), can be used in calculating results such as those shown in Fig. 3 and 4. An approximant such as the (2/3) one given for $F(\xi)$ in the Appendix is also required in calculating $\mathcal{D}_{a^N}$ by the modified cut-off method. When an approximant for $p(\xi)$ derived for $R_1 = 5$ is used to calculate values for ψ_{ao}^N or $\mathcal{E}_{ao}^N$ when $R_1 \neq 5$, almost as high accuracy as with $R_1 = 5$ can be expected when $R_1 > 5$ since, as stated, ψ_{ao}^N depends very little on R_1 alone but primarily on ξ . In particular, $R_1 = 5$ values are very close to $R_1 = \infty$ values of ψ_a^N for a given ξ (18). When R_1 is < 5 , there is somewhat more dependence on R_1 , although the difference is still small even for $R_1 = 2$, the smallest value of R_1 that usually need be considered (18). For example, using the $R_1 = 5$ (3/3) $p(\xi)$ approximant to calculate values of ψ_a^N for $R_1 = 4$ leads to deviations between accurate and approximate values of ψ_a^N which usually occur in the fourth significant figure and rarely in the third. As discussed and listed in ref. (18), even simpler approximants than those given here in the Appendix may ordinarily be used to obtain adequate accuracy in calculated fields and potentials.

In order to achieve high accuracy in the present computer results, we summed such series as those of Eq. [5] to [8] to fairly high order and/or used the epsilon algorithm (21) to extrapolate to accurate final values when necessary. The series are all very rapidly convergent when $\omega < 1$. They are generally most slowly convergent when $\omega = 1$ so we examined this limit. When $\omega = 1$, the series of Eq. [5] is only conditionally convergent. Even so, it generally converges quite rapidly. Thus for $R_1 = 5$, $\Gamma = 1$, and $Z = 1$ we find that ψ_a^N is within 1.7% of its final value when only three (accurate) terms of the series are used. With five terms the percentage is 0.71, and if the epsilon algorithm is used on these five terms, the percentage drops to 0.28.

Since [5] is only conditionally convergent when $\omega = 1$, rearrangement of its terms should change its value. We have found that this circumstance can be put to good use in calculating $\Delta\psi_a^N \equiv \psi_a^N(1) - \psi_a^N(Z_0)$ in the infinite imaging case where $\omega = 1$ and convergence is slowest. Ordinarily this quantity would have to be calculated by two separate evaluations of ψ_a^N using [5]. After a slight rearrangement of the terms of [5], we find the surprising result, however, that

$$\Delta\psi_a^N = \psi_{ao}^N(1; R_1) - \psi_{ao}^N(\rho - 1; R_1) + \sum_{n=1}^{\infty} \{ \psi_{ao}^N(n\rho + 1; R_1) - \psi_{ao}^N[(n+1)\rho - 1; R_1] \} \quad [20]$$

($\omega = 1$ only)

a series whose convergence is still generally good. The above is a lucky result; even it is unnecessary, however, if we note that when $\omega = 1$, $\psi_o^N(Z_0) \equiv 1$. Thus, when $\omega = 1$, $\Delta\psi_a^N$ can still be calculated using [5] only once to first obtain $\psi_a^N(1)$.

In II, we noted the extraordinary constancy of $\mathcal{E}(d)$ for $\beta = 3\text{\AA}$, $\omega = 0$, and $\Gamma = 2/3$ over a wide range of

q . There, Grahame's (22) values for q_1 as a function of q , determined from measurements on a 1N KI electrolyte at 25°C, were used in calculating $\mathcal{E}$. The above result suggested to us that it would be worthwhile to examine the field at the IHP, $\mathcal{E}(\beta)$, for several Γ and ω values. Results are shown in Fig. 5. We have chosen to look at the field at $Z = 1$ since its value at the site of a removed ion is pertinent to ionic polarization, dielectric saturation, and ionic compressibility

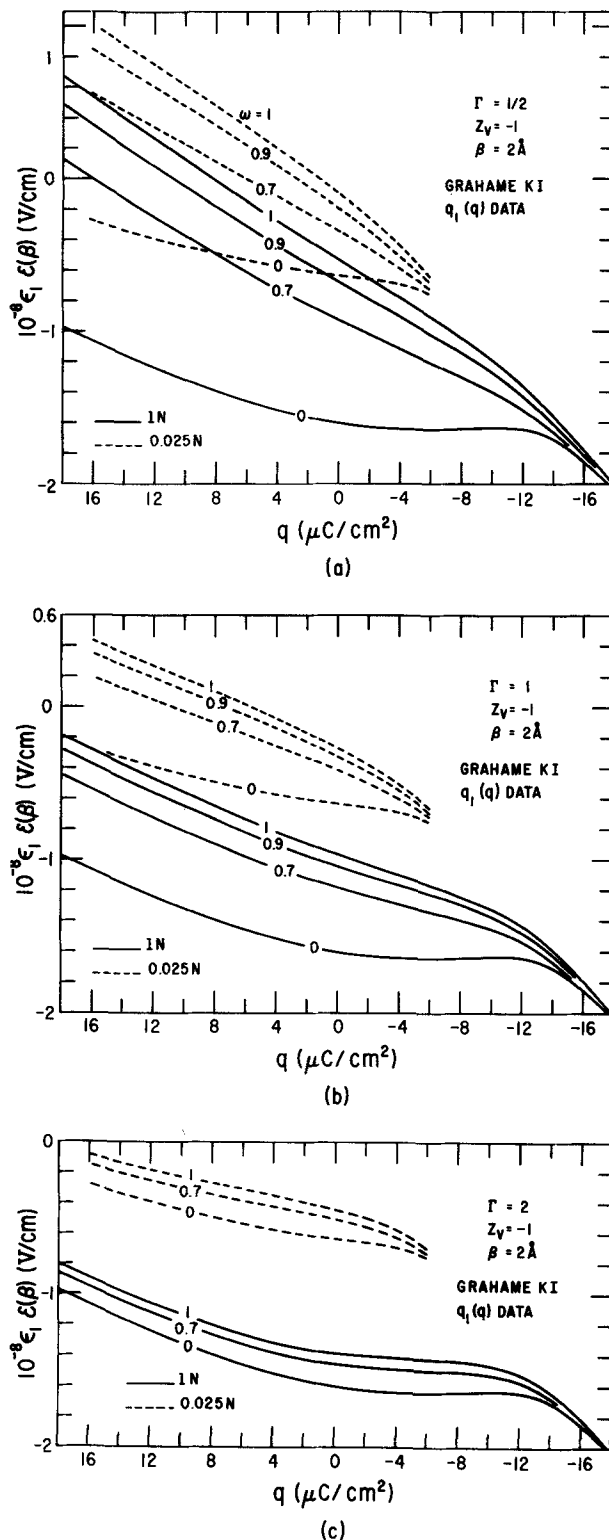


Fig. 5. Full electric field at the IHP, $\mathcal{E}(\beta)$, vs. average electrode charge density, q , using Grahame's KI $q_1(q)$ data for 1N and 0.025N concentrations; $\Gamma = 1/2, 1, 2$; $\beta = 2\text{\AA}$; and several values of ω .

effects (1). We show results in Fig. 5 using Grahame's $q_1(q)$ data for both 1N and 0.025N concentrations for the choice $\beta = 2\text{\AA}$, which we now believe is a more likely value than the $3\text{\AA}$ used in II. The results in Fig. 5 were calculated using the (b) and (c) approximants of Table I in the Appendix. The (b) approximant for $p(\xi)$ is particularly appropriate here since Z is fixed at one for these calculations and R_1 varies. The resulting approximant is therefore somewhat superior to that in (a) where R_1 is fixed at 5 and Z varies to produce changes in ξ . Since $F(\xi)$ is a small correction term, its $R_1 = 5$ approximant is quite adequate in the present case.

It will be seen from Fig. 5 that $\mathcal{E}(\beta)$ remains quite constant when $\omega = 0$ and remains so also even when $\omega \sim 1$ for $\Gamma = 2$. For $\Gamma = 1$, $\mathcal{E}(\beta)$ for the 0.025N concentration goes through zero in the experimental range of q when ω is about 0.4 or greater. Finally, when $\Gamma = \frac{1}{2}$, all of the curves shown change sign in the experimental range except those for $\omega = 0$. If we assume that the Γ appropriate to the actual experimental situation is 1 or less and that $0.7 < \omega \leq 1$, then it is evident that $\mathcal{E}(\beta)$ will vary sufficiently over the q range, for either 1N or 0.025N concentrations, that it will not be a good assumption to take ϵ_1 completely saturated and equal to 6 over the entire q range. For $\Gamma = 1$, $\omega = 0.9$, and this constant value of ϵ_1 , the appropriate curve shows that $\mathcal{E}(\beta)$ varies from about 3.5×10^7 v/cm to 4×10^6 v/cm as q goes from -18 to $+18$ $\mu\text{C}/\text{cm}^2$. With ϵ_1 becoming less saturated and thus larger as $\mathcal{E}(\beta)$ decreases (20), $\mathcal{E}(\beta)$ at $q = 18$ $\mu\text{C}/\text{cm}^2$ might be as small as 2×10^6 v/cm. We remark again, however, that the introduction of an ϵ_1 at all in the present situation is a considerable approximation, making any conclusions about its variation uncertain.

Figure 6 shows the nonlinearity parameter Δ_0 for the usual values of Γ and many positive values of ω . These results form a bridge between the $\omega = 1$ results of I and the $\omega = 0$ results of II. Here and elsewhere in this paper all $\omega = 1$ and $\omega = 0$ results agree excellently with those previously given in I and II. We can now follow in detail the continuous change from one limiting case to the other, however. It should be noted that in the present paper the ω values 0 and 1 represent only limiting situations and are not examined in detail; more results for these specific values thus appear in I and II than are given here.

It will be noted from Fig. 6 that, except for ω values equal to or very near unity, Δ_0 is by no means negligible over most of the range of R_1 shown. At the top of Fig. 6a is shown a q_1 scale following from the R_1 scale when $\beta = 2\text{\AA}$, probably a reasonable value for the KI system. The $R_1 = 2$ value, which is the smallest possible R_1 for close-packed spherical adions, corresponds to a q_1 of 115.6 $\mu\text{C}/\text{cm}^2$ for this choice of β . On the other hand, the largest value derived from Grahame's (22) experiments is about 43 $\mu\text{C}/\text{cm}^2$ (corresponding to $R_1 \approx 3.3$ for $\beta = 2\text{\AA}$), indicating a maximum adion surface coverage of about 37% for these experiments.

The dashed and dotted lines of Fig. 6b are calculated for the usual cut-off model of the inner region (8c, 18), not for a hexagonal array. They use values of ψ_{a0}^N obtained from Eq. [A-1] with constant p values, and [A-1] is applied for all Z and R_1 combinations since [A-4] is only applicable to the hexagonal array. The dotted-curve value $p = (\sqrt{3}/2\pi)^{1/2} \approx 0.5250376$ is Grahame's original figure. It is the value appropriate for a smeared array of charges and is thus also the value for the fixed hexagonal array when $\xi \rightarrow \infty$. It is the smallest value of p possible for such an array. The dashed-curve value $p = 4\pi/\sigma\sqrt{3} \approx 0.65752059$, where $\sigma \approx 11.034175$, is the value appropriate for an array of ideal dipoles when $\xi \rightarrow 0$ [see ref. (18)]. This p is thus the largest value possible with a hexagonal array. It is interesting that over much of the R_1 scale of interest, the accurate

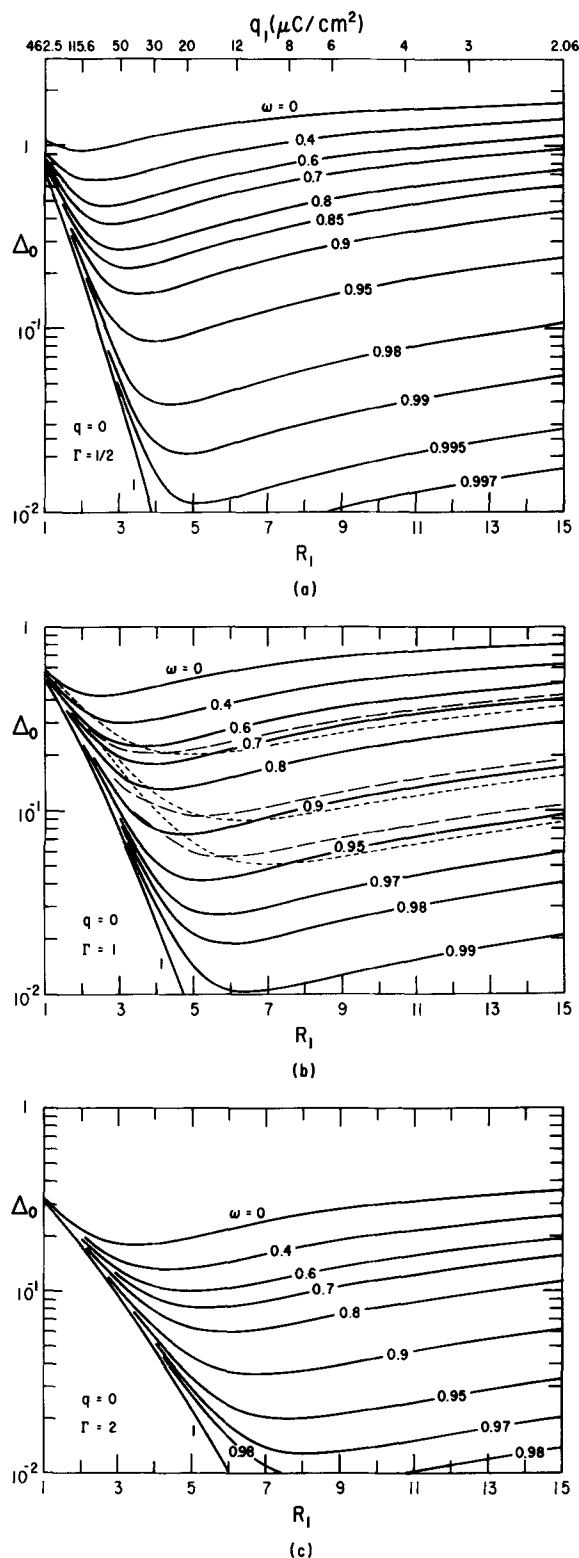


Fig. 6. The nonlinearity parameter Δ_0 vs. R_1 for $\Gamma = \frac{1}{2}, 1, 2$ and positive values of ω . Dotted lines were calculated using Grahame's cut-off model involving the constant value of p , $p \approx 0.5250376$. Dashed lines were calculated similarly with p again constant and equal to $p_0 \approx 0.65752059$. The nonlinear q_1 scale at the top of (a) is applicable for the choice $\beta = 2\text{\AA}$ only.

hexagonal-array results lie between those obtained with the above two limiting values of p . On the other hand, in the region of appreciable IHP charge density, say $2 \leq R_1 \leq 6$, where the fixed hexagonal array model is most appropriate at room temperature, we note regions of very appreciable deviation of the

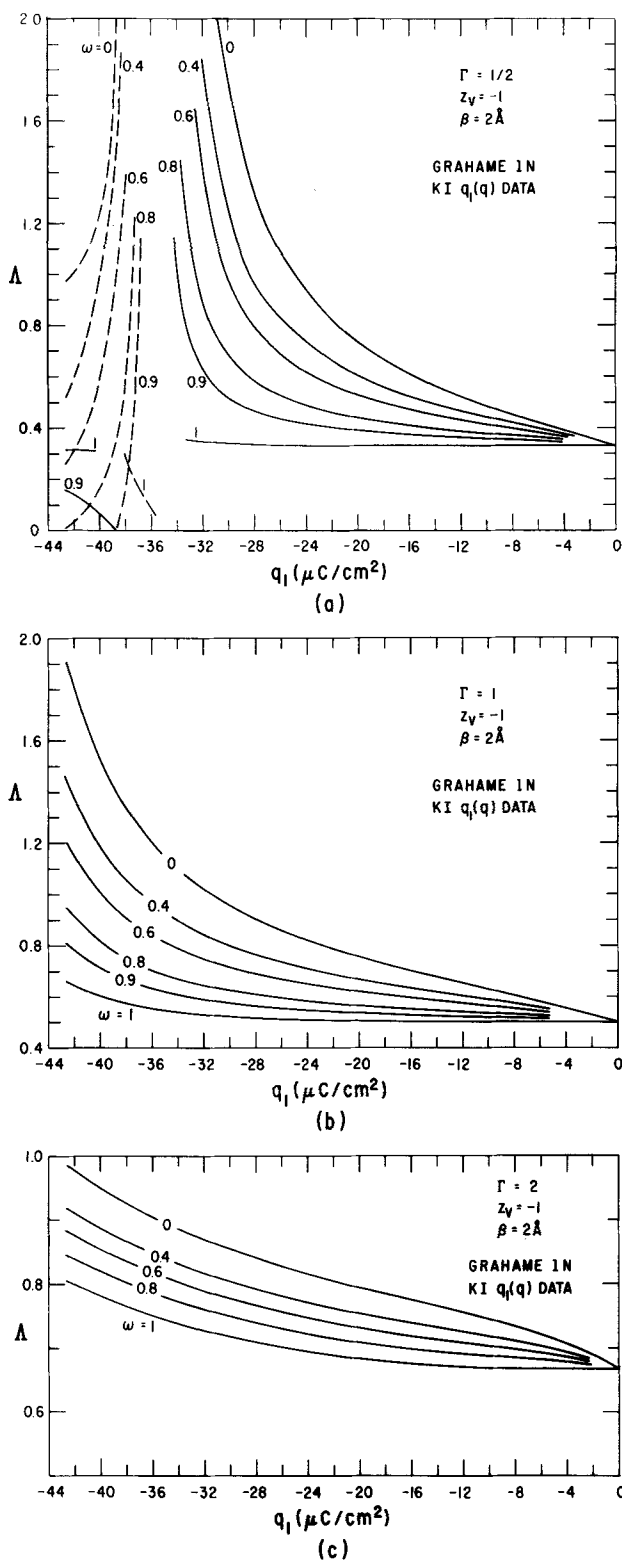


Fig. 7. Quantity $\Delta \equiv \psi_1/V_1$ vs. Grahame's derived $q_1(q)$ for $\beta = 2\text{\AA}$, $\Gamma = 1/2, 1, 2$, and several positive values of ω . Dashed lines denote negative values.

fixed- p results from the hexagonal array results. In such a region, the hexagonal model is definitely preferable to a constant- p cut-off model. The exact charge density where the latter might be more preferable is difficult to determine [see (7, 17)], however.

Figure 7 shows the ratio of the micropotential to the macropotential, $\Delta \equiv \psi_1/V_1$, vs. q_1 for $\Gamma = 1/2, 1$, and 2, and several values of ω . Here again Grahame's (22) $q_1(q)$ values for 1N KI were employed in calcu-

lating Δ from Eq. [17]. For a given q , the corresponding q_1 was used to calculate R_1 , using $\beta = 2\text{\AA}$, then $\Delta\psi_a^N$ was calculated and was finally used in Eq. [17]. This calculation of $\Delta\psi_a^N$, and also most of those for Δ_0 in Fig. 6, used the $R_1 = 5$ (3/3) approximant for $p(\xi)$ discussed in the Appendix together with Eq. [A-1] and [A-4]. We do not show Δ curves for the 0.025N concentration, but calculations for this case showed them to be quite similar to the 1N curves. We have elected to show Δ curves here instead of the corresponding Δ curves given in I and II because Δ turns out to be very appreciable for most of the curves (nonlinear distance dependence of ψ^N) and the ratio Δ is itself then of most direct interest.

Equation [17] shows that when $\Delta = 0$, $\Delta = \lambda$. This is, of course, the case at the right of the Δ curves in Fig. 7 where $q_1 \approx 0$. Dashed lines are used in Fig. 7a to indicate negative values of Δ . These arise because V_1 may change sign, leading to a pole in Δ near $q_1 = -35 \mu\text{C}/\text{cm}^2$. Although both ψ_1 and V_1 are continuous, their ratio need not be. The peculiar behavior of the $\omega = 1$ curve in Fig. 7a is evidently produced by a zero in ψ_1 near but not at that of V_1 .

The quantity of most interest for adsorption isotherms is ψ_1 itself. It can, of course, be readily obtained from the Δ values given here by multiplying by calculated values of V_1 . In this paper, we shall not be directly concerned with adsorption isotherms and with the ψ_1 which enters them, reserving such discussion for another place (17). It is worthwhile to point out, however, that when Δ is neglected (often a good approximation for infinite imaging) and ψ_1 is then taken as λV_1 , Grahame (22) and Grahame and Parsons (23) have found that the ψ_1 derived by using experimental results in a simple adsorption isotherm leads to a variable λ . Although this specific approach can probably be improved, it does lead to λ variation with q or q_1 of much the same form as that of Δ in Fig. 7b and c. In particular, λ is found to increase continuously for KI as q increases from $-18 \mu\text{C}/\text{cm}^2$ to $18 \mu\text{C}/\text{cm}^2$. Reasonable values of Γ and ω can even be selected that lead to Δ variation quantitatively very similar to that found for λ , but we do not wish to stress this agreement even though the Grahame-Parsons $\lambda (= \psi_1/V_1)$ determined as above is formally fully equivalent to our Δ and they both equal the constant λ (a ratio of distances) of the present paper when $q_1 = 0$.

Dielectric ESP

While in the foregoing work metallic imaging is assumed to occur at a conducting electrode and dielectric imaging at the OHP, our mathematical model also pertains approximately to an entirely different system: At an electrolyte-dielectric interface, we may also have a surface phase in which ions are hexagonally arrayed on an "IHP." Separating this phase from the bulk electrolyte would be an "OHP;" separating it from the bulk dielectric would be an "ESP." While external charged electrodes might be present near the surface layer, producing a uniform field ψ_e , these electrodes need only be a microscopically large distance removed from the layer (a probable situation here) for their effect upon ψ_a to be negligible.

Our model in the present situation is that the OHP approximates to a metallic imaging plane and the ESP forms a dielectric imaging plane. Clearly, the OHP will approximate better and better to a conductive imaging plane the higher the concentration of ions in the diffuse layer. To maintain our previous equations with minimum change requires that we now define β as the IHP-OHP separation, γ as the IHP-ESP separation, q as the total surface charge density on the OHP, that we measure z from the OHP (thus $z = \beta + \gamma$ at the ESP), and that we define ϵ_1 and ϵ_2 to be the effective dielectric constants of the surface phase and bulk dielectric, respectively (see Fig. 8).

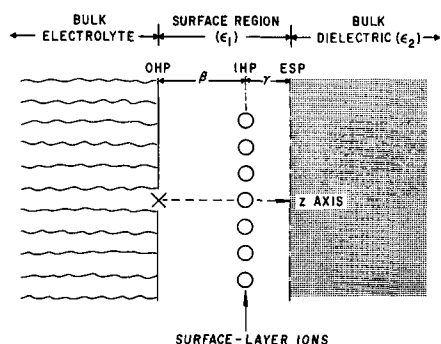


Fig. 8. Cross-sectional diagram showing appropriate situation and distances when the OHP is taken as a conducting plane.

There still remain certain differences between our system and the original compact layer for which our equations were derived. Most important of these is that the anion density on the IHP will now depend on the potential difference between the IHP and the conductive plane; thus, $\psi_1 \equiv \psi(\beta) - \psi(0) \equiv \psi(\beta)$, where " β " here is probably numerically equal to the " γ " of our original system. The reason for the present involvement of the conductive plane potential, which is of course zero, is that in this system the ions are presumed to originate (again neglecting V_2) from the conductive (outer Helmholtz) plane whereas earlier they originated from the dielectric imaging plane, and there the finite potential at the dielectric discontinuity had to be incorporated in the micropotential. Finally, apart from the numerical differences expected between new and old β 's, γ 's, q 's, and so forth, we may now obtain with greater likelihood negative values for the parameter ω . Levine *et al.* (7b, 11) have discussed, to some extent, a situation where ϵ_2 is taken as 15, pertaining to silver chloride, and ϵ_1 taken as 10 or 15. In these cases, $\omega = 0.2$ and 0, respectively. On the other hand, the important air-electrolyte interface is a more common situation. For $\epsilon_1 = 10$ and 5, ω is about -0.82 and -0.67 , respectively, for such a boundary.

We have already plotted in Fig. 3 and 4 normalized discrete potentials and displacements for $q = -q_1$ and negative values of ω . To make use of these curves in the present situation, however, we must interpret the plane marked OHP in those figures as being the ESP, and the plane $\xi = 0$, in the earlier case the ESP, as the OHP. The IHP is the same in both situations. The different interpretations now given to β and γ result in probable changes in the numerical values appropriate to these quantities; correspondingly, the numerical value of ψ_∞ is likely to be different. Note that if the numerical values of γ and β are simply interchanged in going from a conductive ESP to a dielectric ESP situation, then Γ in the dielectric situation has a magnitude which is just the reciprocal of that in the usual situation. Although we have only shown curves of potential and field applying when $q = -q_1$, the extension to the more general case is straightforward. The expression for ψ_e in the present situation is identical to that given for the case of a conducting electrode.

Finally, we wish to define and calculate a quantity Λ analogous to that defined for our original system. In the present situation, we shall again define

$$\Lambda \equiv \psi_1/V_1 = \psi(\beta)/V_1 = \psi^N(1)/V^N(Z_0) \\ = \frac{[1 + (q/q_1)] - \psi_a^N(1)}{\Gamma + (1 + \Gamma)(q/q_1)} \quad [21]$$

This equation shows that when $q_1 \neq -q$ $\Lambda \rightarrow (1 + \Gamma)^{-1} = Z_0^{-1} = \Gamma^{-1}\lambda$ as $R_1 \rightarrow \infty$ for fixed q . Specializing now to the case most interesting and pertinent for the present situation, $q = -q_1$, we find $\Lambda = \psi_a^N(1)$,

just the discrete-charge contribution to the normalized potential at the IHP. The choice $q = -q_1$ means that the charge on the IHP is entirely balanced by that in the diffuse layer, here taken to be on the (conducting) OHP. One would only expect $q \neq -q_1$ in the present situation when the inner layer was exposed to an externally applied field.

We have plotted curves for Λ vs. R_1 in Fig. 9. For completeness and because some authors have taken

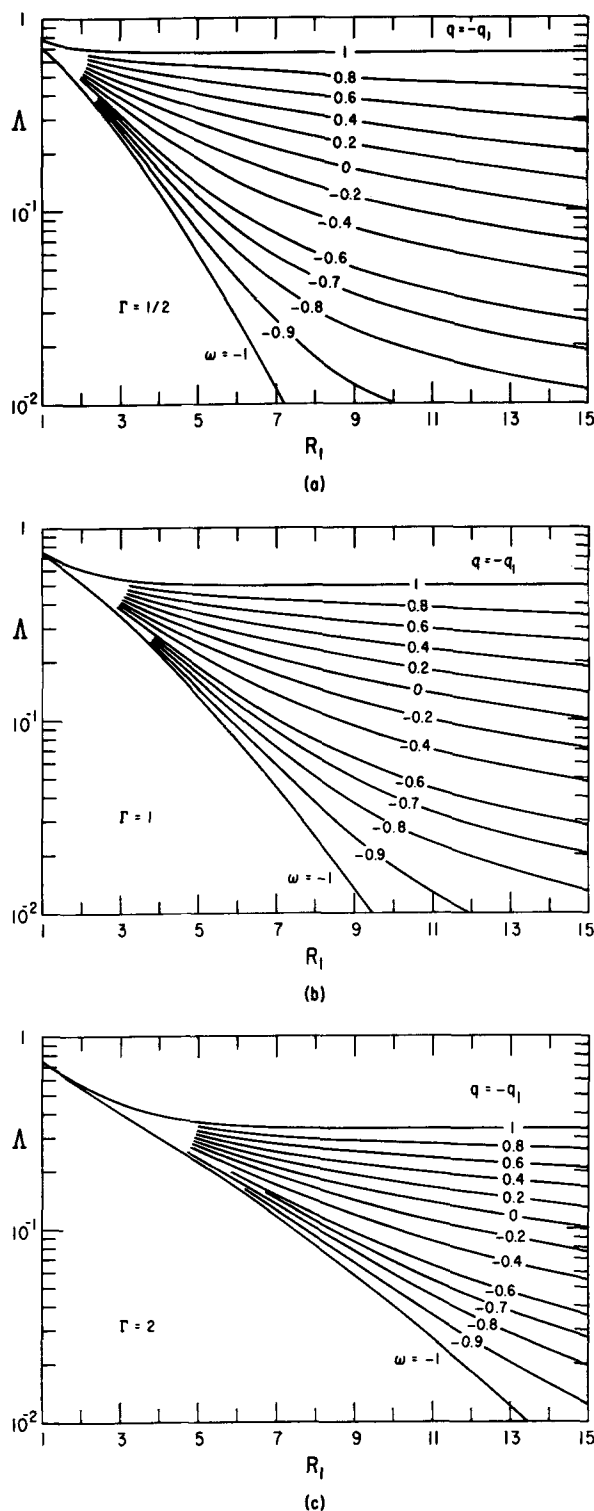


Fig. 9. Quantity $\Lambda \equiv \psi_1/V_1$ appropriate when the OHP is taken conducting vs. R_1 for $\Gamma = 1/2, 1, 2$ for a full range of ω values. Here $q = -q_1$ and $\Lambda = \psi_a(\beta)/\psi_\infty$ pertinent to the conducting ESP case as well.

the OHP to be a metallic imaging plane in situations where the material beyond the ESP may lead to a positive value for ω , we show curves for positive ω values as well as negative ones. It will be noted that as R_1 increases all the $\omega = 1$ curves approach the limiting value $(1 + \Gamma)^{-1} = \beta/(\beta + \gamma)$. In this situation, $\psi_1 = \psi_a(\beta)$ is just the proper linear proportion, $\beta/(\beta + \gamma)$, of $V_1 = \psi_a$ and Δ , here defined through $\Delta \equiv \Gamma^{-1}\lambda(1 + \Delta)$, would be zero as it should be. Again, we have presented curves of Δ rather than Δ since we believe Δ to be more significant in the present case.

The curves of Fig. 9 are particularly valuable since when $q = -q_1$, $\Delta = \psi_a(\beta)/\psi_a$, and the curves show immediately how large the discrete-charge potential at the IHP is compared to the total potential (at large distances) set up by the array, ψ_a . These results for $\psi_a^N(1)$ are, of course, just as appropriate for the situation of a conducting ESP discussed in the last section since they immediately give the relative ψ_a at the IHP in this case as well. Note further that since the average potential at the IHP, $V(\beta)$, is also ψ_a for $q = -q_1$, the curves show in addition how $\psi_a(\beta)$ differs from the average potential at the IHP.

In the present paper, we have made calculations based on a model in which there is one conductive imaging plane and one dielectric imaging plane (and have also included results appropriate for two conducting planes). These calculations were referred to two physical situations. In the first situation treated, the electrolyte was assumed to behave like a simple dielectric, mobile ions in the diffuse layer were not explicitly taken into account, and the OHP therefore was considered a dielectric imaging plane. In the second situation, the OHP was considered effectively to be a conductive imaging plane, and the dielectric imaging occurred elsewhere, at the surface of a true dielectric. How valid is our model for these two situations?

The theoretical difficulties associated with the first system have already been discussed somewhat and preclude a precise answer to this question for this case. However, we may make some reasonable guesses as follows. Inasmuch as the ions in the diffuse layer will cause the OHP to become to some extent a conductive imaging plane, we anticipate that the present model will not accurately portray the first system except possibly at ionic concentrations so low that the effective Debye lengths are larger than other characteristic dimensions of the system (e.g., β and r_1), concentrations which are often lower than those of most interest. Note that the Debye length for 0.025N at 25°C is about 20Å. If $\beta = 2\text{Å}$, this corresponds to $R_1 = 10$, and complete neglect of any diffuse layer conductive imaging would probably then only be justified for R_1 values appreciably smaller than 10 for this bulk concentration. Although one might be tempted to apply the present model by using an effective ω , larger than that calculated on the basis of dielectric constants alone, which hopefully would approximately take into account the mobile ions, we do not here advocate this procedure as an entirely satisfactory solution to the problem for two reasons: Our own estimates of the importance of conductive imaging at the OHP for ionic concentrations such as 1N would imply effective ω values exceedingly close to unity, for which the Ershler model is appropriate. Furthermore, any actual small difference between the predictions of the Ershler model and those of the present model with $\omega \approx 1$ would probably be no larger than the errors introduced into the present treatment by the attempt to subsume the action of the diffuse-layer ions into an effective ω . Nevertheless, the present approach adequately illustrates for the first time the effects of the ever-present underlying dielectric imaging.

Concerning the second system considered, where the OHP is taken to be a conductive imaging plane, our

evaluation of the model validity is accordingly considerably higher. The foregoing arguments which favor taking the OHP as just such an imaging plane are as encouraging in this situation as they were discouraging in the former one. We therefore feel that the present treatment pertains to a dielectric ESP (for the usual appreciable ionic concentrations) fairly well. If an accurate future theory should demonstrate that our present opinions are overestimates of conductive imaging at the OHP, then we would have to interchange our evaluations of the applicability of the present model to the two situations.

Acknowledgment

The authors greatly appreciate the help of Marilyn White and Charles Ratliff in writing the several computer programs used in this work.

APPENDIX

In another paper (18), we have discussed in some detail how Grahame's (8c) cut-off approximation for single imaging discreteness-of-charge potential calculations can be modified in a simple way to yield highly accurate results for hexagonal planar arrays of ideal or non-ideal dipoles. Here, we thus shall only quote results used in the present work.

For ψ_{ao}^N and $\mathcal{G}_{ao}^N$ we may write

$$\psi_{ao}^N = \frac{1}{2} \{ [(pR_1)^2 + (Z+1)^2]^{1/2} - [(pR_1)^2 + (Z-1)^2]^{1/2} \} \quad [\text{A-1}]$$

$$\mathcal{G}_{ao}^N = \frac{1}{2} \left\{ \frac{Z+1 - [(pR_1)^2/Z]F}{[(pR_1)^2 + (Z+1)^2]^{1/2}} - \frac{Z-1 - [(pR_1)^2/Z]F}{[(pR_1)^2 + (Z-1)^2]^{1/2}} \right\} \quad [\text{A-2}]$$

In these equations, p and F (which are constant and zero, respectively in Grahame's work) are primarily functions of $\xi \equiv Z/R_1$ but depend slightly on R_1 as well (18). Here $F \equiv -d\ln p/d\ln \xi$. Using Chebyshev rational function approximation methods, we obtained in ref. (18) very accurate, yet simple, approximations of the p and F functions which make [A-1] and [A-2] exact for hexagonal arrays. This method of approach was used because it was found that p changed only over a limited range for any fixed R_1 when ξ varied from 0 to ∞ and F was small over most of the range, reaching a maximum of about 0.14 near $\xi = 1$.

The rational function approximations for p and F are all of the type

$$f(\xi) = \sum_{i=0}^n a_i \xi^i / \sum_{i=0}^m b_i \xi^i \quad [\text{A-3}]$$

and may be termed (n/m) approximants. Note that $b_m \equiv 1$. In Table I we give the coefficients of (3/3) and (0/2) approximants for $p(\xi)$ and of a (2/3) approximant for $F(\xi)$. Coefficients of other simpler approximants are given in ref. (18). Here, we have used more complicated approximants than would normally be necessary in order to ensure accuracy of at least several decimal places in all the results calculated. In Table I, (a) values are for a fit which min-

Table I. Rational function coefficients for (a) $p(\xi)$ ($R_1 = 5$ fit), (b) $p(\xi)$ ($Z = 1$ fit) and (c) $F(\xi)$ ($R_1 = 5$ fit)

i		(a) $\delta_R = 1.355 \times 10^{-4}$ (c) $\delta_A = 3.965 \times 10^{-3}$		(b) $\delta_A = 1.261 \times 10^{-3}$	
		a_i		b_i	
0	(a)	-41.607035		-63.857680	
	(b)	9.2168220		9.4332222	
	(c)	0		-3.3093430	
1	(a)	27.059236		41.149777	
	(b)	0		0.72151658	
	(c)	-0.21087153		6.4039198	
2	(a)	-33.039613		-59.285095	
	(b)	0		1.0	
	(c)	0.058259894		-5.2036756	
3	(a)	0.75227306		1.0	
	(b)	0		0	
	(c)	0		1.0	

imized the absolute value of the relative deviations, δ_R , while (b) and (c) values were for fits which minimized the absolute values of the absolute deviations, δ_A , between accurate values and approximate predictions. Values of the pertinent δ_R and δ_A 's are shown in the table and illustrate the high accuracy of the approximants.

We have used the above expressions for ψ_{ao}^N and $\mathcal{E}_{ao}^N$ for a hexagonal array for $Z < 1 + 3R_1$. When $Z \geq 1 + 3R_1$, however, the results of II reduce to

$$\psi_{ao}^N \cong 1 - (\sqrt{3}/4\pi) [R_1^2/(Z^2 - 1)] \quad [A-4]$$

and

$$\mathcal{E}_{ao}^N \cong (\sqrt{3}/2\pi) [ZR_1^2/(Z^2 - 1)^2] \quad [A-5]$$

accurate to about eight figures when $Z = 1 + 3R_1$ and becoming even more accurate as Z/R_1 increases further. Therefore, these simple expressions were employed in place of [A-1] or [A-2] when $Z \geq 1 + 3R_1$.

GLOSSARY

Basic Parameters of System

e	Charge of proton
q_1	Average surface charge density on IHP
q	Total surface charge density on conductive plane
z_v	Effective valence of surface-layer ions
ϵ_1	Effective dielectric constant of surface region
ϵ_2	Effective dielectric constant of dielectric region
β	Distance from IHP to conductive plane
γ	Distance from IHP to dielectric imaging plane
d	$\beta + \gamma$ = thickness of surface region
r_1	Lattice spacing of surface-layer ions
ω	$(\epsilon_2 - \epsilon_1)/(\epsilon_2 + \epsilon_1)$
η	$1 + \omega = 2\epsilon_2/(\epsilon_2 + \epsilon_1)$
λ	$\gamma/(\beta + \gamma)$
Γ	γ/β
ρ	$2d/\beta$
(x, y)	Coordinates in a plane parallel to IHP, generally set to zero here
z	Coordinate of position normal to ESP
Z	z/β
R_1	r_1/β
Z_0	$1 + \Gamma = d/\beta$
ξ	$Z/R_1 = z/r_1$

Unnormalized Potentials and Fields

ψ	$\psi_a + \psi_e \equiv$ actual potential at a point (x, y, z)
ψ_e	Portion of potential arising from a uniform electric displacement
ψ_a	Portion of potential arising from discrete system of charges and images
ψ_{ao}	Discrete potential in single image regime
ψ_{acc}	Discrete potential in infinite image regime
$\mathcal{E}$	Actual electric field, associated with ψ
$\mathcal{E}_a$	Field associated with ψ_a
$\mathcal{E}_{ao}$	Field associated with ψ_{ao}
$\mathcal{D}_a$	Displacement associated with ψ_a

Potential Differences, Average Quantities, and Normalizing Factors

ψ_1	Micropotential $\equiv \psi$ (at IHP) $-\psi$ (at OHP)
V_1	Average potential drop across surface layer
V_2	Potential drop across diffuse layer
$V(z)$	Average potential in a plane $z = \text{constant}$
ψ_a	$(4\pi\beta q_1/\epsilon_1) =$ average potential drop arising from discrete array of charges and images; used as a normalizing factor
ϵ_a	Normalizing quantity for fields $\equiv -\psi_a/\beta$
ϕ_a	Normalizing quantity for displacements $\equiv \epsilon_1 \mathcal{E}_a$

Normalized Potentials and Fields

ψ^N	ψ/ψ_a
ψ_a^N	ψ_a/ψ_a
ψ_{ao}^N	ψ_{ao}/ψ_a
ψ_e^N	ψ_e/ψ_a
ψ_1^N	ψ_1/ψ_a
V_1^N	V_1/ψ_a
$V^N(Z)$	$V(z)/\psi_a$
$\Delta\psi_a^N$	$\psi_a^N(1) - \psi_a^N(Z_0)$
$\mathcal{E}^N$	$\mathcal{E}/\mathcal{E}_a$
$\mathcal{E}_a^N$	$\mathcal{E}_a/\mathcal{E}_a$
$\mathcal{E}_{ao}^N$	$\mathcal{E}_{ao}/\mathcal{E}_a$
$\mathcal{E}_e^N$	$\mathcal{E}_e/\mathcal{E}_a$
$\mathcal{D}_a^N$	$\mathcal{D}_a/\mathcal{D}_a$

Other Quantities

Λ	$\psi_1/V_1 \equiv$ a quantity measuring ratio of micro-potential to full surface layer average p.d.
Δ	A quantity measuring departure from a strict proportionality between ψ_1 and V_1 . When the ESP is conductive, $\Delta \equiv \lambda(1 + \Delta)$; when the ESP is dielectric, $\Delta \equiv \Gamma^{-1}\lambda(1 + \Delta)$
Δ_0	Value of Δ for $q = 0$
p, F	Quantities used in our modified cut-off approximation for ψ_a and $\mathcal{E}_a$

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4. C. A. Barlow, Jr., and J. R. Macdonald, *ibid.*, **43**, 2575 (1965). The colon in ref. (2) of this paper should be a semicolon; $\mathcal{E}$ in the Glossary should be $\mathcal{E}_a$; there should be a hyphen between "average" and "discrete" at the bottom of p. 2586; and Mignolet (28) on p. 2590 should be Mignolet (14).
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Discussion

H. D. Hurwitz: It must be stressed that the value of the micropotential is not sufficient to account for the total coulombic interaction among adsorbed particles. This is shown easily by deriving, as indicated next, the total coulombic energy of interaction for a set of charges of species α adsorbed at the inner Helmholtz plane (IHP), assuming as usual that: 1, the interaction α -solvent is implicitly stated in the definition of the local dielectric constant ϵ_0 and of the pair correlation function $g_{1,2}$ introduced below; 2, the interaction α -diffuse layer charge is described by a simple average electrostatic effect in which the ionic distribution in the diffuse layer is smeared out over parallel planes to the electrode; 3, the dielectric discontinuity near the outer Helmholtz plane (OHP) leads to partial or total reflection of the charge e_α of α .

Under these conditions we assume that the surface density of α is p_α . Hence $p_{\alpha 1}$ gives the probability to find α at one given position, 1, of the IHP. The probability to encounter a neighbor to α at position 2 is then by definition $g_{1,2} p_2$ where $g_{1,2}$ is the radial distribution function. The coulombic interaction between these two particles is $(e^2_\alpha/\epsilon_0)\gamma_{1,2}$ where $\gamma_{1,2}$ represents the reduced coulombic potential at 2 corresponding to an isolated charge located at the IHP at 1. The quantity $\gamma_{1,2}$ includes the effects of partial or total infinite reflections into the dielectric discontinuities of the model.

The probable pair interaction for positions 1 and 2 is

$$\frac{e^2_\alpha}{\epsilon_0} \gamma_{1,2} g_{1,2} p_{\alpha 1} p_{\alpha 2} \quad [1]$$

Let us sum over all particles on the IHP considered to interact with α at 1 and over all central positions, 1, in order to get finally the total interaction energy

$$\frac{e^2_\alpha}{2\epsilon_0} \sum_1 \sum_2 \gamma_{1,2} g_{1,2} p_{\alpha 1} p_{\alpha 2} \quad [2]$$

(Because of symmetry of $\gamma_{1,2}$ $g_{1,2}$ the quadratic sum is divided by 2.) Instead of summing over all 1 and 2 we may integrate over-all distances s_{12} between 1 and 2 and over-all positions 1 in order to get finally

$$\Omega \frac{e^2_\alpha}{2\epsilon_0} \int g_{1,2} \gamma_{1,2} p^2_\alpha ds_{12} \quad [3]$$

where Ω is the total area of the IHP.

The change of interaction energy on introduction of one particle α is obtained through differentiation of [3]. Therefore

$$\frac{e^2_\alpha}{2\epsilon_0} \int \gamma(s_{12}) \frac{\partial}{\partial p_\alpha} (g(s_{12}) p^2_\alpha) ds_{12} \quad [4]$$

It is clear that [4] is the contribution of coulombic interactions among specifically adsorbed charges to the change of potential energy of adsorption. A more convenient way to write [4] is to decompose this expression in the following manner

$$e_\alpha \left[p_\alpha \frac{e_\alpha}{\epsilon_0} \int \gamma(s_{12}) ds_{12} + p_\alpha \frac{e_\alpha}{\epsilon_0} \int \gamma(s_{12}) [g(s_{12}) - 1] ds_{12} \right] + \frac{1}{2} p^2_\alpha \frac{e^2_\alpha}{\epsilon_0} \int \gamma(s_{12}) \frac{\partial}{\partial p_\alpha} g(s_{12}) ds_{12} \quad [5]$$

In view of the fact that the first term in [5] corresponds to the effect at [1] of charges uniformly distributed over the IHP, it is readily inferred that by definition this term pertains to the average electrostatic potential (macroscopic potential).

The second term is then a correction which results from discreteness-of-charge effects [$g(s_{12})$ is different from unity] and the first and second term together represent the so-called micropotential.

At this point we have to realize that whenever we introduce in our system at position 1 an ion α we do not alter only the local density p_α , but we modify simultaneously the radial distribution of particles. This in turn gives rise to some interaction energy. The last term of [5] reflects such an effect of radial redistribution. The contribution of this effect to the free energy of adsorption has yet been considered only from a qualitative viewpoint^{1,2} and is generally neglected. However, a careful evaluation based on a simple model for $g_{1,2}$ has led³ to the conclusion that such work of redistribution is not negligible at all and may even be of the order of magnitude of the discreteness-of-charge correction as given by the second term in expression [5]. In the crude hexagonal lattice approximation of Ershler, in which no allowance is made for thermal motion, the $g_{1,2}$ functions are represented by delta Dirac functions.

C. A. Barlow, Jr.: Three points seem to have been raised here. First, "that the value of the micropotential is not sufficient to account for the total coulombic interaction among adsorbed particles;" second, "that the work of redistribution is not negligible at all and may even be of the order of magnitude of the discreteness-of-charge correction;" and third, that the hexagonal lattice approximation is crude, the use of exact two-particle correlation functions being preferable.

We disagree with the first point; however, the disagreement possibly stems merely from a different use of words: We assert⁴ that the total coulombic energy $U(N)$ of a system of N charges is given by a sum over all particles of the local potential times one-half the charge; in other words, we agree entirely with Dr. Hurwitz's Eq. [2] within the approximation of the model. Now except for a contribution, V_2 , from the diffuse layer, the "local potential" occurring above is just the micropotential. To equate the two involves the neglect of V_2 in the micropotential, to be sure, but this is discussed in our present paper just after Eq. [14], and this doesn't seem to be Dr. Hurwitz's objection. His objection, as seen from the second point raised, is that we are somehow neglecting rearrangement energy. This is not true; in the first place, in the present paper we did not need to calculate the energy of adsorbing one additional ion, $\Delta U \equiv U(N+1) - U(N)$. We have shown explicitly⁴ that, having found the micropotential, we have a means of calculating the related quantity $U(N)$ in accordance with the foregoing. In the second place, our approach does lead to the redistribution energy in essentially the same way that it arises in Dr. Hurwitz's discussion when one finally gets down to the business of calculating ΔU , the energy of adsorption. The only difference in approach is that we initially calculate $U(N)$ and save the differencing with respect to N until the very last (as may be seen from our papers^{5,6} where we determine the total energy for adsorbing an additional

¹ D. C. Grahame, *Z. Elektrochem.*, **62**, 264 (1958).

² C. A. Barlow, Jr. and J. R. Macdonald, *J. Chem. Phys.*, **43**, 2575 (1965).

³ H. D. Hurwitz, *Z. physik. Chem.*, To be published.

⁴ C. A. Barlow, Jr. and J. R. Macdonald, *J. Chem. Phys.*, **43**, 2575 (1965).

⁵ J. R. Macdonald and C. A. Barlow, Jr., "The Penetration Parameter for an Adsorbed Layer of Polarizable Ions," *J. Appl. Phys.*, To be published in 1966.

⁶ J. R. Macdonald and C. A. Barlow, Jr., *Can. J. Chem.*, **43**, 2985 (1965).

ion). We agree with Dr. Hurwitz's statement about orders of magnitude; we were, in fact, the first to make a correct quantitative study of redistribution energy in the present system. Indeed, although this question was considered quantitatively by us in the work cited by Dr. Hurwitz⁴ and a curve plotted to show the numerical magnitude of the effect for a wide range of surface coverages, in his discussion Dr. Hurwitz only references his own unpublished work to support "the conclusion that such work of redistribution is not negligible at all and may even be of the order of magnitude of the discreteness-of-charge contribution." It is of interest to note that in our previously published work⁴ we explicitly state that the work of redistribution is of the same order of magnitude as the full adsorption energy and is not at all negligible. Dr. Hurwitz seems to have missed noticing the significance of the quantity η in our paper,⁴ since he refers to this paper as considering the question "only from a qualitative viewpoint." Further quantitative treatment of this matter will soon appear.⁵

Finally, that the hexagonal model may be "crude" cannot be denied. We have already presented a discussion of just how crude it may be under some conditions.⁶ If the proper correlation functions were known, they would certainly be preferable to the δ -function lattice model. They are not known, however, so our approach has been to try to keep the following statement (concerning statistical physics) of Richard Feynman⁷ in mind:

"Anyone who wants to analyze the properties of matter in a real problem might want to start by writing down the fundamental equations and then try to solve them mathematically. Although there are people who try to use such an approach, these people are the failures in this field; the real successes come to those who start from a physical point of view, people who have a rough idea where they are going and then begin by making the right kind of approximations, knowing what is big and what is small in a given complicated situation. These problems are so complicated that even an elementary understanding, although inaccurate and incomplete, is worth while having...."

We believe the hexagonal array approach to be the "right kind of approximation" for a q_1 range of practical importance.⁶

Richard Payne: According to the results in Fig. 7, the ratio of ψ_1/V_1 is uniformly larger for the single imaging limit than for the infinite imaging limit. This does not seem consistent with the Esin and Shikov and Grahame calculations for the single imaging case which overexplained the Esin and Markov effect (i.e., ψ_1/V_1 too small); whereas Ershler's treatment of the infinite imaging case gave larger values of ψ_1/V_1 . It seems, therefore, that the trend in Fig. 7 as ω varies is inverted.

J. Ross Macdonald and C. A. Barlow, Jr.: The apparent discrepancy pointed out by Dr. Payne is not significant for several reasons. First, the single-imaging treatments of Esin and Shikov and Grahame not only treat a physically very different situation than the present single-imaging one but the situation treated is much less physically appropriate than is ours. Second, we properly include the uniform D field contribution to the single-imaging micropotential, omitted by other authors. The Esin-Shikov and Grahame treatments are not really single-image ones at all since they consider fixed arrays of adsorbed ions each with a rigidly paired counterion in the diffuse layer. The counterions are not taken as images of the adions but as real associated ions at a fixed perpendicular distance from the

adions. Ershler has modified this approach by considering single imaging of the adions in the diffuse layer, a preferable assumption. This is indeed a single-imaging treatment, but it necessarily still disagrees with our $\omega = 0$ results in Fig. 7 since there we take imaging in the electrode instead of the solution, take q variable, and include the D field contribution.

The significant point regarding Fig. 7 is that for reasonable Γ values the $\omega = 1$ curves generally yield micropotential values which are smaller than they should be to explain the Esin-Markov effect (Δ too small) while the $\omega = 0$ results yield micropotentials which are too large to explain it. For an appropriate value of Γ , it appears possible to pick a ω value near but less than unity which will lead to results which will explain the Esin-Markov effect (within the limitations of the present treatment) better than will results with either $\omega = 1$ or 0.

Richard Payne: It is not clear why grounding of the electrode should affect the charge on the metal since the whole system is electrically neutral. If the effect of grounding the electrode were to eliminate the uniform displacement component ψ_e , then it would be possible to determine the point of zero charge simply by measuring the potential of the grounded electrode with respect to a reference electrode.

J. Ross Macdonald and C. A. Barlow, Jr.: Actually one could not measure the ecm potential in this way without additional information about the system: The condition that the electrode is grounded is not the same as the condition of zero charge. The charge on the electrode which produces the ground condition depends on the imaging situation which applies, as well as the adsorbed surface charge density. Specifically, for single and for dielectric imaging the condition is that $q = -q_1$, whereas for infinite-conductive imaging

we have $q = -\frac{\gamma}{\beta + \gamma} q_1$ at the ground condition. How-

ever, if one knew the physical (imaging) situation and measured q_1 with the electrode grounded, one might be able to infer from the average potential drop across the compact layer what the ecm potential is.

Richard Payne: I think it is important to point out that λ in the Grahame-Parsons analysis is not fully equivalent to ψ_1/V_1 in this treatment as stated by the author for the following reason. In the Grahame-Parsons analysis λ is obtained from the experimental results by investigating the concentration dependence of the adsorption energy at constant charge in the electrode. λ is therefore an average value over a range of concentrations and amounts adsorbed. In other words, the imaging conditions in the diffuse layer are not kept constant during the calculation whereas the calculations given here refer to definite imaging conditions in the solution.

J. Ross Macdonald: Our $\Delta \equiv \psi_1/V_1$ is formally equivalent, as stated, to Grahame and Parson's $(\psi^i - \psi^o)/\psi^u$, which they set equal to λ on the basis of an approximate infinite-imaging treatment. Experimental results seem to indicate that the ratio $(\psi^i - \psi^o)/\psi^u$ depends only slightly, if at all, on the concentration. It therefore seems reasonable to compare our theoretical results, which assume a definite degree of dielectric imaging at the OHP, with experimentally derived results obtained using various concentrations. We do not expect much change of ω with concentration, and the change in the average charge density in the diffuse layer apparently does not affect the ratio with which we compare appreciably. The comparison thus appears useful even though there are approximations involved which preclude perfect agreement between theory and experiment.

⁷ R. Feynman, R. B. Leighton, and M. Sands, "The Feynman Lectures on Physics," Vol. I, p. 39-2, Addison-Wesley, Reading, Mass. (1963).

Richard Payne: The authors have pointed out that the value of λ (and hence ψ_1) obtained in the Grahame-Parsons analysis is dependent on an assumed form of the isotherm which I think is an important point. Incidentally, I would also like to point out that λ also depends on whether the anion activity or the salt activity is used in the isotherm.

In this context, it seems to me that the Frumkin isotherm or better the Flory-Huggins modification of the Frumkin isotherm introduced by Parsons offers an excellent starting point for the experimental study of discreteness of charge effects for the following reasons. If we write down the Stern form of the isotherm,

$$\frac{\theta}{1-\theta} = a_{\pm} \exp [(\psi_1 + \Phi)F/RT] \quad [1]$$

and compare this with the Frumkin isotherm in the form

$$\frac{\theta}{1-\theta} = \frac{a_{\pm}}{\Gamma_s} \exp \left[-\frac{\Delta G^0}{RT} + f(q) - A\theta \right] \quad [2]$$

it seems reasonable to equate the specific adsorption potential Φ with the standard free energy of adsorption at zero coverage $-\Delta G^0$, i.e.

$$F\Phi = -\Delta G^0 - \ln \Gamma_s \quad [3]$$

and to write ψ_1 as

$$\frac{F\psi_1}{RT} = f(q) - A\theta \quad [4]$$

where $f(q)$ is the form of the charge dependence of the standard free energy of adsorption at zero coverage and A is the lateral interaction coefficient of the adsorbed anions. I think it is clear from [4] that the Frumkin isotherm with a constant value of A represents the infinite imaging limit to a close approximation since the adsorption energy is linearly dependent on the amount adsorbed. Deviation from the linear θ dependence of the lateral interactions, e.g., a $\theta^{3/2}$ dependence for single imaging should show up as variation in A when the Frumkin isotherm is applied. It is interesting to note that apparent variation of A is often found for adsorption of anions from solutions of a single salt.

A further point I would like to make here is that the infinite imaging case also leads to linear charge dependence of $-\Delta G^0$ providing the effect of replacement of oriented solvent dipoles is neglected and providing the dielectric constant is assumed constant:

$$\begin{aligned} \psi_1 &= \frac{\gamma}{\beta + \gamma} V_1 = \frac{\gamma}{\beta + \gamma} \cdot \frac{4\pi}{\epsilon} \left[q + \frac{\gamma}{\beta + \gamma} \cdot q^1 \right] \beta + \gamma \\ &= \frac{r\pi\gamma}{\epsilon} q + \frac{4\pi}{\epsilon} \cdot \frac{\gamma^2}{\beta + \gamma} \cdot q^1 \end{aligned}$$

Deviations from the linear charge dependence of $-\Delta G^0$ can arise (i) from replacement of oriented dipoles which would contribute a term $4\pi n\bar{\mu}/\epsilon$ to V_1 where n is the number of dipoles replaced by each ion and $\bar{\mu}$ is the mean normal component of the dipole moment and (ii) through deviations of ψ_1/V_1 from constancy resulting from imperfect imaging in the solution.

J. Ross Macdonald and C. A. Barlow, Jr.: We do not agree that ψ_1 is given by $\frac{\gamma}{\beta + \gamma} V_1$ only that the uni-

form field part is given by this quantity in the infinite-conductive imaging situation. The linearity of ψ_1 with charge on the electrode, q , is independent of this, however, and in fact does not depend on the type of imaging present. We only refer to the explicit dependence of ψ_1 on q . Since evidently as q changes q_1 will generally change as well, we do not include all q -depend-

ence in the present discussion. We are in fact referring to the linearity of ψ_1 with q under hypothetical circumstances where the constitution of the compact layer is held fixed and only q is allowed to change. Accordingly, we agree with the statement that ψ_1 will be explicitly linear with q , but disagree with the reasoning which led to this conclusion and with the comments concerning causes for "deviations from the linear charge dependence of $-\Delta G^0$." On the other hand, the remarks about "deviations . . . (etc.)" are interesting and pertinent if by "charge dependence" is meant "dependence on q_1 ." Note, however, that if one is concerned with the dependence of ψ_1 on q_1 , he must include the contribution from the discrete ions and their images (ψ_a), and that such inclusion will itself destroy the linearity without the additional help of the two effects cited by Dr. Payne.

Roger Parsons: I think it is fair to say that the general idea of the discreteness of charge effect is widely accepted and is supported by several pieces of experimental evidence. However, it is much more difficult to demonstrate experimentally the fine details of the models proposed, e.g., whether imaging is partial or infinite, whether the hexagonal lattice or the disordered models provide the closest approximation to reality. I should emphasize the importance of attempting to verify these models by experimental test. We have tried to examine imaging in the diffuse layer recently⁸ and suggest that it is not complete. However, this work does not test the efficiency of imaging in the dielectric jump.

In connection with the problem of thermal motion, is it correct to say that some of the difference between you and Levine *et al.* is due to the fact that you assume a lower dielectric constant in the inner layer? A value of 6 or 7 seems more reasonable than 15.

I would like to point out that the variable λ obtained by Grahame and Parsons was further analyzed by Parry and Parsons⁹ and an improved model suggested.

Finally, I think it is interesting to note that the elegant method of summation proposed in this paper has some relation to the intuitive way in which David Grahame discussed the potential drop in the inner layer¹⁰.

J. Ross Macdonald and C. A. Barlow: We believe this difference of opinion as to the proper value of the dielectric constant to use in these circumstances is the only significant disagreement between Levine and his co-workers and ourselves although there are small perturbations on the final numbers for lattice stability coming from slight differences in stability criteria, etc. In a recent paper by Bell, Mingins, and Levine¹¹ the inner-layer dielectric constant is taken to be 10. As you have pointed out we have generally taken 5 or 6 to be more typical of the inner-layer dielectric constant, to the extent that one can define such an object. This choice was motivated by our prior work on differential capacitance in the electrical double layer. However, in later theoretical studies on electrode work function change, we calculate that the dielectric constant in some systems may be completely different from bulk values insofar as work function effects are concerned. The significant phrase is "insofar as work function effects are concerned." It turns out that the use of a single dielectric constant to characterize dielectric effects in the inner layer is incorrect, since this region is so completely different from three-dimensional bulk matter. We have re-

⁸ E. Dutkiewicz and R. Parsons, *J. Electroanal. Chem.*, **11**, 100 (1966).

⁹ J. M. Parry and R. Parsons, *Trans. Faraday Soc.*, **59**, 241 (1963).

¹⁰ Fig. 5 in *Z. Elektrochem.*, **62**, 264 (1958).

¹¹ Bell, Mingins, and Levine, *Trans. Faraday Soc.*, **62**, 949 (1966).

cently estimated the dielectric constant effective in reducing the lateral interaction between adions and find that it is no greater than 2, and more likely to be closer to unity. So you see the question of the proper dielectric constant to use is a rather confused one. It seems to us that all previous estimates of lattice stability in the inner-layer (including our own) have employed a dielectric constant which is at least 3 times too large, and possibly much worse than that.

It is completely correct that our image summation method stems from that originally used (for $\omega \equiv 1$) by Grahame. We have generalized the approach to include the $|\omega| < 1$ case. In this connection, we think it is interesting to note a certain difficulty not fully

appreciated by Grahame which troubled us for a while: Whereas the summation technique used here is absolutely convergent for all $|\omega| < 1$, the series is only conditionally convergent for $\omega = 1$. As it happens, the particular arrangement of terms employed by Grahame and ourselves in the $\omega = 1$ case leads to the potential appropriate for $q = -q_1$. Since this does not coincide with the condition $q = -\gamma q_1/(\beta + \gamma)$ obtaining when both imaging planes are at zero potential, this accounts for Grahame's conclusion that the infinite set of images and the adions contribute to the total p.d. across the inner layer, an incorrect conclusion for the model with conductive imaging at the OHP.

The Adsorption of Aromatic Sulfonates at a Mercury Electrode

II. Sodium p-Toluenesulfonate—An Example of Two-Position Adsorption

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ABSTRACT

The adsorption of the p-toluenesulfonate ion on a mercury surface from aqueous solution has been studied by measuring the interfacial tension and the capacity of the electrode as a function of concentration. An interpretation of the results is proposed in terms of two orientations of the adsorbed ion. A simple model of this type of system is proposed, at first neglecting interaction between adsorbed ions other than due to their space-filling properties. A very approximate allowance for interaction is introduced, and it is concluded that consideration of interaction is essential for a full description of the system.

In the previous paper of this series (1), we described the adsorption of the benzene m-disulfonate (BMDS) ion which may be treated by methods closely analogous to those used for simple ions such as the halides. This is essentially because adsorption of this ion occurs with the plane of the benzene ring oriented parallel to the plane of the mercury solution interface over the whole of the experimentally accessible range. As we mentioned previously, the behavior of the p-toluenesulfonate (PTS) ion is more complicated and, as we shall show in the present paper, it cannot be analyzed by using the surface pressure in a simple way. This is due to the existence of the adsorbed species in more than one orientation, and we believe that this system provides a clear-cut example of two position adsorption. This problem has been discussed in a qualitative way by Damaskin *et al.* (2); here a more quantitative description is attempted.

Experimental

Measurements of differential capacity and interfacial tension were carried out as described previously (1). Sodium p-toluenesulfonate was recrystallized three times from equilibrium water; it crystallizes as the hemihydrate from concentrated solutions. The water content was determined by heating and weighing and also volumetrically after exchanging the Na^+ for H^+ on an ion exchange resin.

Results

The concentration dependence of the capacity at constant temperature is shown in Fig. 1. It is evident from these data that the behavior of PTS is qualitatively different from that of BMDS as shown in Fig. 1 of ref. (1). At the lower concentrations up to 0.1M the capacity curves for both ions are similar in showing a marked peak at a potential of about -0.6V (SCE). However, as the concentration is increased above 0.1M this peak is lowered, eventually being

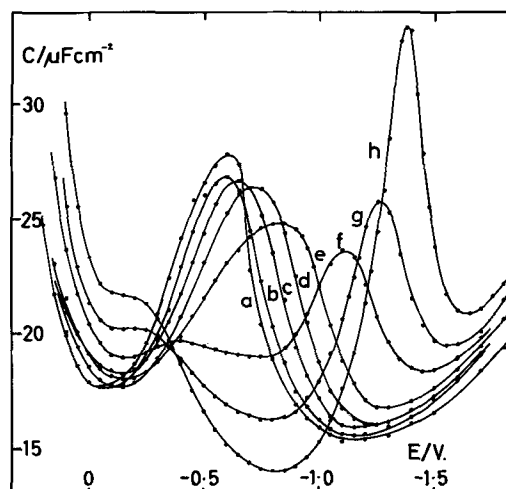


Fig. 1. Differential capacitance per unit area of a mercury electrode in aqueous solutions of sodium p-toluenesulfonate at 30°C plotted as a function of potential with respect to a saturated calomel electrode: a, 0.0113M; b, 0.0227M; c, 0.0567M; d, 0.113M; e, 0.227M; f, 0.567M; g, 1.134M; h, 2.268M.

replaced by a minimum, while a higher and narrower peak develops at more negative potentials (up to -1.4V vs. SCE). These results suggest that at low bulk concentrations the PTS ion is lying flat on the mercury surface like the BMDS ion while at higher concentrations re-orientation occurs to allow closer packing of the PTS ion.

The capacity curves were integrated numerically using a digital computer (Elliott 803) as described previously (3). The integration constants were obtained from the electrocapillary curves and are given in Table I. The potential of zero charge was found from the electrocapillary curve by extrapolating the

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