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EQUILIBRIUM DOUBLE-LAYER THEORY

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Abstract—Those electrolyte double-layer theories are reviewed and compared which involve detailed consideration of charge and potential conditions in the double-layer region. Separate consideration is given to those calculations where it may be a good approximation to treat all charges as continuously distributed and those where discreteness-of-charge effects must be invoked. Three conditions are analyzed: (1) that where there is no specific adsorption and the (solvent) molecules in the monomolecular inner region of the double layer are all of the same type and close-packed; (2) specific ionic adsorption; and (3) specific adsorption of neutral substances. It is shown how previous treatments of (1) may be improved by including induced molecular polarization and average planar dipolar interaction effects. Careful attention is given to the calculation of the field which orients dipoles in the inner layer, and it is pointed out how the inclusion of planar depolarization alters the approach to dielectric saturation. Errors, defects, and simplifications in earlier continuous-charge treatments of specific ionic adsorption are discussed. Some difficulties arose from failure to distinguish properly mean fields, based on the continuous-charge approximation, and fields derived from the micropotential, a quantity derived from discreteness-of-charge considerations. It is concluded that presently available phenomenological treatments of specific ionic adsorption and the micropotential are inadequate since they generally involve improper calculations of the micropotential, ignore various charge discreteness effects, and employ oversimplified statistical mechanics. Comparison of previous treatments of specific adsorption of neutral substances again shows unwarranted simplification. In particular, it does not appear that the dipole moment and/or dielectric constant of adsorbed molecules can be extracted with any confidence by applying current theory to experimental data. An improved treatment of the problem is outlined which makes use of an approximate formula of Frumkin that treats unadsorbed and adsorbed regions in the double-layer separately but which is here generalized by coupling such regions together by planar interaction. Finally, a statistical treatment of the discrete adsorption problem is briefly described which is more nearly correct than the usual Boltzmann expressions in those situations where competition and saturation effects are important.

1. INTRODUCTION

IN THIS paper, we shall review some recent theoretical treatments of the electrolyte double layer adjoining a plane metallic electrode and shall outline new approaches to certain parts of this problem. For simplicity, we shall consider only a uni-univalent electrolyte and an ideal polarized electrode. Only a fixed, static distribution of charges and dipoles will be analyzed; thus, all differential capacitances which enter must be understood as applying in the limit of low frequencies where kinetic effects are zero and charging and discharging are quasi-equilibrium processes.

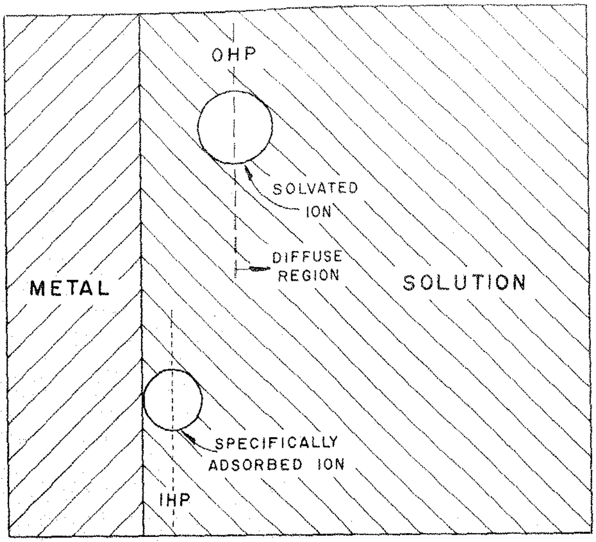

FIG. 1. Double-layer structure.

A diagram of double-layer structure is presented in Fig. 1. It is frequently convenient to separate the region adjoining the electrode into two sections, an inner layer which may or may not contain specifically adsorbed ions and an outer, diffuse layer where solvated ions are held in average positions by the balance between diffusive forces and the electric field. When ions of a single type are specifically adsorbed, the inner layer itself may be separated into two parts by the inner Helmholtz plane (IHP), the locus of the center of charge of chemisorbed ions. Similarly, the outer Helmholtz plane (OHP) is the plane of nearest approach of the electrical centers of solvated ions and marks the beginning of the diffuse region.

There is good evidence that in the absence of specific adsorption the inner region consists of a close-packed monomolecular layer of solvent molecules only.[1-5] Its total thickness, d, will then probably be the sum of a fraction of an angstrom from the surface atoms of the metallic electrode,[3, 4, 6] the diameter of a solvent molecule, and the radius of the major ion type in the diffuse layer. When cations and anions are of different sizes, d will thus vary depending on whether the first layer of the diffuse region is primarily populated by cations or anions; however, such variation is frequently a small fraction of the total thickness and is usually neglected.

A solvated ion retains its first shell of oriented solvent molecules much more strongly than subsequent shells.[7, 8] Thus, it is reasonable that a solvated ion at the OHP should be separated from the electrode by only a single solvent molecule. The process of specific adsorption then involves the loss of the hemisphere of solvation toward the electrode and the consequent approach of the ion to within approximately an ionic radius of the surface.

In the present work, we shall consider the double layer without specific ionic adsorption, with specific ionic adsorption, and with adsorption of surface-active neutral substances. Most discussion of previous work will be given in the text, but for the convenience of readers who wish to refer to original papers, minor printing errors, etc., observed in these papers will be noted after their reference. Further, the Appendix presents a table comparing notation used by various workers, and a comparison of numerical values actually used or suggested for several pertinent double-layer quantities.

As Grahame and Parsons[9] have pointed out, in the final analysis the double layer must be considered as a three-dimensional problem and the interactions of all charges in solution and on the electrode considered simultaneously. In the absence of a complete solution to this forbidding task, it has been found useful to make the approximation of splitting the problem into two parts, a part for which it seems a good approximation to consider continuous distributions of charge and a part where the discrete nature and specific positions of charges must be considered. Continuous charge distributions have been primarily employed to calculate double-layer capacitance at a fixed (possibly zero) amount of specific adsorption. On the other hand, the discrete nature of the actual charge distribution has been invoked in calculating specific adsorption itself and in improving the theory of the diffuse region. In the present work, we shall also make use of the above continuous-discrete separation. It has been pointed out a number of times, however, that corrections to the usual Gouy–Chapman theory of the diffuse layer[10-16] and to Debye–Hückel theory[17-19] make a negligible change in the overall differential capacitance of the double layer, the usual experimental quantity. We shall, therefore, follow most other writers on the full double layer containing both an inner and a diffuse region and use simple diffuse-layer theory for this region. Earlier reviews of parts of the present subject may be found in Refs. 4 and 20 through 24. Their fullness makes it unnecessary for us to consider all aspects of double-layer theory in detail, and we shall therefore concentrate on a comparative study of a few recent non-thermodynamic approaches.

2. CONTINUOUS CHARGE DISTRIBUTIONS

2.1. No specific adsorption. Stern[25] was the first to suggest that because of the finite size of ions, the diffuse double layer did not extend all the way up to the electrode and that the total capacitance* of the double layer could therefore be considered as the series combination of the capacitance of the inner, charge-free region and that of the diffuse layer. As mentioned in the last Section, however, when ions are not specifically adsorbed it is presently commonly agreed that the thickness of the charge-free region, d, includes that of (at least) a single solvation shell as well as contributions from ionic size and possible field penetration into the first layer of electrode surface atoms.[3,4,6]

In the absence of specific adsorption, let $\tilde{C}_1$ and $\tilde{C}_2$ be the differential capacitances of the inner, charge-free region and of the diffuse region, respectively. Then $\tilde{C}$, the total double-layer differential capacitance, will equal $(\tilde{C}_1^{-1}+\tilde{C}_2^{-1})^{-1}$. Using the Gouy–Chapman theory of the diffuse layer for $\tilde{C}_2$, Grahame[20,26] has employed experimental values of $\tilde{C}$ and the applied potential difference to calculate $\tilde{C}_1$ vs. total mean electrode charge, q. It is found as shown in Fig. 2 that the resulting $\tilde{C}_1$ varies strongly with q, and Grahame[27] and others suggested qualitatively that such dependence might arise from compression and partial dielectric saturation of the inner layer, whose material is exposed to a very high electric field at appreciable $|q|$.

The above derivations of $\tilde{C}_1$ were carried out using aqueous electrolyte with fluoride as the anion because it was felt[20, 28] that fluoride ions remained hydrated and were not specifically absorbed even on strong anodic polarization. Devanathan[29] has suggested, however, that fluoride ions may

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* All extensive terms such as capacitance, charge, etc., are to be understood to refer to unit area.

indeed be specifically adsorbed. Further, it has been suggested by the authors,[3,4] by Watts-Tobin[30], and by Mott and Watts-Tobin[6] that the rapid increase in $\tilde{C}$ with anodic polarization in fluoride solutions may arise from a specific adsorption process involving fluoride ions, hydroxyl ions, or adatoms. Clearly, in the charge regions where specific adsorption is present, the $\tilde{C}_1$ obtained by Grahame's method will not be that of a charge-free region, and, in fact, the series combination of the two capacitances used will then be incorrect as well, as discussed later.[31] Mention should finally be made of Frumkin's[32] observation that the anodic rise in NaF and CsF is considerably reduced if purification is carried out in a Teflon rather than glass vessel.

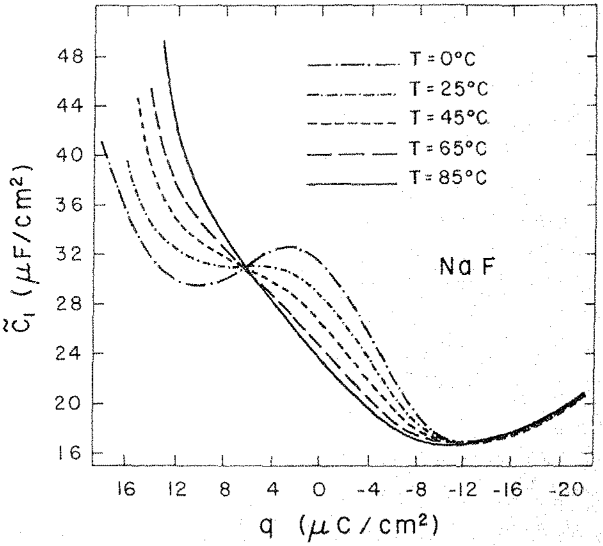

FIG. 2. Differential capacitance of the inner layer, $\tilde{C}_1$, calculated by Grahame from his experimental results using a mercury electrode and assuming no specific adsorption.

For cathodic polarization there is little or no specific adsorption of fluoride ions and none of cations such as sodium or potassium, at least until nearly the limit of cathodic polarization is reached. Further, the shape of $\tilde{C}$ curves for $q < \sim -10 \mu C/cm^2$, where the ions at the OHP interface are almost entirely cations, is almost independent of the cation involved.[33] In fact, it turns out that C_{1s}, the integral or static capacitance of the inner layer, is about 10 per cent larger for CsCl than for LiCl, although the crystallographic radius of Cs is much larger than that of Li, and d_0 may thus be expected to be about 25 per cent larger for CsCl than for LiCl.[*] Mott, Parsons, and Watts-Tobin[34] have explained the near constancy of the $\tilde{C}$ curves in this region of cathodic polarization by the assumption that the dielectric constant in the inner region rises sharply toward the bulk solvent value at the surface of hydrated ions rather than at their charge centroids, as is more commonly assumed. This would render d_0 virtually independent of cation radius but would not explain the observed effect of a larger differential and static capacitance with a larger cation. Perhaps the observed result is also associated with the likelihood[34] of weaker hydration for larger ions, making their effective d_0's smaller than those of smaller ions.

An approach quite different from Grahame's was employed by one of the authors[2] (Ref. 2 will be referred to as I). There, the effect of high electric fields in the inner region on compressing the layer and saturating its dielectric constant was explicitly introduced. It was then possible to calculate directly the dependence of $\tilde{C}_1$ on potential across the inner layer and, on using diffuse layer theory, to calculate $\tilde{C}$. With some rearrangement of the original work, the total mean p.d. across the double layer, V_0, can be written as the sum of that across the inner layer and that across the diffuse region, yielding

$$V_0 = \frac{4\pi qd}{\varepsilon_1} + \left(\frac{2kT}{e}\right)\sinh^{-1}\left(\frac{q}{2A}\right), \tag{2.1.1}$$

where the zero of V_0 is so chosen that $V_0=0$ at $q=0$, the electrocapillary maximum (ecm), and e is the magnitude of the electronic charge. Note that here V_0 will be positive when the electrode charge q is positive. The quantity $A \equiv kT\varepsilon_s/4\pi eL_D$, where ε_s is the dielectric constant of the solution, and the Debye length $L_D \equiv (kT\varepsilon_s/8\pi c_0 e^2)^{1/2} = 1{\cdot}9881 \times 10^{-10}\,[T\varepsilon_s/N]^{1/2}$ cm, where T is the absolute temperature, N the normality of the solution, and c_0 the concentration of positive or negative ions in the solution far away from an electrode.

Since both d and ε_1, the static dielectric constant of the inner region, are taken dependent on E_1, the constant field in this layer, we also require the relation $D_1 = \varepsilon_1 E_1 = 4\pi q$. Given E_1, one can then calculate ε_1, d, q, and then V_0. Finally, $\tilde{C}$ may be obtained from $\tilde{C}^{-1} = \mathrm{d}V_0/\mathrm{d}q$; the result is complicated and need not be given, especially since $\tilde{C}$ is easily calculated with a digital computer using differences.

The specific dependence of d on E_1 used was

$$d/d_0 = (1+\beta P)^{-1}, \tag{2.1.2}$$

where

$$P = \varepsilon_1 E_1^2/8\pi. \tag{2.1.3}$$

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[*] Here d_0 is the value of d at zero electrical pressure.

Here the pressure P is that arising only from the compressive effect of the attraction of the charged capacitor "plates" formed by the electrode and diffuse layer. Equation (2) involves the compressibility parameter β, is properly linear for $\beta P \ll 1$, and yet requires infinite pressure to yield zero thickness.

The following expression for ε_1, proposed by Grahame,[35] was used,

$$\varepsilon_1 = \varepsilon_\infty + (\varepsilon_1^0 - \varepsilon_\infty)\,[\sinh^{-1}(\sqrt{2b}\,E_1)/(\sqrt{2b}\,E_1)], \tag{2.1.4}$$

where ε_1^0 is the value of ε_1 when there is no dielectric saturation, ε_∞ is its value when the dipolar contribution to ε_1 is fully saturated out, and b is a dielectric saturation constant.

Using the above equations, Grahame's [36] $\tilde{C}$ data for NaF at 25°C and several solute concentrations was fitted by adjustment of the parameters ε_1^0, β, and b. At the ecm, the data gave [2,37] $\varepsilon_1^0/d_0 \cong 3{\cdot}3$ Å^{-1}; the assumption of a monolayer of water led to a thickness d_0 of about 4·6 Å, finally yielding $\varepsilon_1^0 = 15$. The quantity ε_∞ was taken as 5, based on independent high-frequency measurements. Fitting of the data was carried out only for $q \leqslant 0$ and was relatively simple since the effects of different values of β and b interacted only slightly. Not only was quite accurate fitting of the data found to be possible in this region where specific adsorption could be presumed absent but also the final values of β and b were in order of magnitude agreement with results obtained by entirely different methods for bulk water. In the actual comparison of theory and experiment, dielectric saturation of ε_s by the field in the diffuse layer was also included. The inclusion of this effect, which is only one of the corrections to Gouy-Chapman theory possible, made less than one per cent difference in the theoretical curves and so has been omitted from the present discussion.

When Grahame's[26] later measurements of $\tilde{C}$ for NaF at a variety of temperatures became available, the present authors[3,4] improved a number of points in the above theory and fitted this data as well (Ref. 4 will be referred to as II). First, the earlier theory gave $\tilde{C}$ curves symmetrical about the ecm, in contradistinction to experiment, and hence could not fit $q > 0$ data simultaneously with $q \leqslant 0$ data. In II it was attempted to avoid part of this difficulty by introducing an effective or "natural" field,*[38] $\mathcal{E}_n$, which gave a small amount of dielectric saturation (dipole orientation) even at the ecm and allowed the maximum ε_1 to occur at small

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* This field was denoted by E_0 in II. Here we shall usually use script E's for effective fields solely orienting and polarizing dipoles and italic E's for average fields.

positive (or negative) values of q. Such orientation was later also suggested by Parsons[24] and by Watts-Tobin.[30]

In II, it was suggested that dipole orientation in the absence of an external field might arise from some or all of the following factors: permanent multipole moments higher than the dipole, an induced dipolar moment, non-spherical molecule, electrode electron wave-function overlap and bonding, the non-planarity of the metallic surface on an atomic scale, and differences in dipole image reflection in the mercury and in the diffuse layer. Parsons,[24] on the other hand, suggested as reasons a greater specific attraction of one end of the water molecule to the mercury than the other, the dipolar layer within the metal surface, or the fitting of the surface water layer into the remainder of the water structure. Watts-Tobin[30] has invoked the quadrupole moment of a water molecule in a detailed way to explain the initial orientation, and finally Mott and Watts-Tobin[6] have suggested that water molecules in the inner layer are surrounded by mercury atoms, surely an extreme case of mercury surface non-planarity.

Parsons[24] has criticized I because he states it suggests that d at the ecm (d_0) is proportional to the radius of the cation. This is not so. The theory of I was applied only for $q \leqslant 0$; in the absence of specific adsorption it was expected that over most of the q range investigated cations would greatly exceed anions in the first layer of the diffuse region. Thus, a cation radius was included as a part of d_0 but amounts to less than 25 per cent of the full d_0 used in I. Going from Na^+ to K^+, an increase in radius of about 40 per cent, is reflected as only about an 8 per cent change in d_0. A change of similar magnitude in d_0 occurs for NaF when Na^+ is replaced by F^- in going from cathodic to anodic polarization. In a detailed theory some such interpolation formula for the effective ion-radius contribution to d_0 as $[r_+\exp(-V_2^*)+r_-\exp(V_2^*)]/2\cosh V_2^*$ might be used, where $V_2^* \equiv eV_2/kT$ and V_2 is the p.d. across the diffuse layer.

One difficulty with the theory of I is that equation (2.1.4) does not exhibit the proper high field behavior. In the limit of high fields, the dipoles of the solvent molecules in the monomolecular inner layer may be expected to be all lined up in the field direction, making the permanent dipolar polarization a maximum. Since further polarization is impossible (omitting change of shape effects), the term multiplying $(\varepsilon_1^0-\varepsilon_\infty)$ in (2.1.4) must decrease as E_1^{-1}, yielding a constant polarization for sufficiently high fields. Since (2.1.4) does not give such behavior when $\sqrt{(2b)}E_1 \gg 1$, it has been replaced in II by

$$\varepsilon_1 = 1+\lambda^n(\varepsilon_\infty-1)+\lambda^r ah(E), \qquad (2.1.5)$$

$$h(E) \equiv \tan^{-1}(\sqrt{[b]}E)/(\sqrt{[b]}E), \qquad (2.1.6)$$

where $a \equiv \varepsilon_1^0 - \varepsilon_\infty$ and $E \equiv E_1 + \mathcal{E}_n$. The saturation term $h(E)$ is again taken from Grahame's work[35] and now exhibits proper high field behavior. In addition, the new equation incorporates an experimentally necessary dependence on density. In equation (2.1.5) $\lambda \equiv \varrho/\varrho_0 \equiv d_0/d = (1+m\alpha P)^{1/m}$, where ϱ is the density of the inner region, ϱ_0 is its value at $P=0$, and α is a compressibility constant. Insofar as its density dependence is concerned, (2.1.5) represents a generalization and improvement of the Owen–Brinkley equation,[39] just as the above equation of state for ϱ represents a generalization and improvement of the Tait equation of state.[40] The constants n, r, and m were usually taken as 1, 0, and 1, respectively, in II on the basis of reasonable arguments. Note that this choice still leaves some density dependence of ε_1, in distinction to (2.1.4) which includes none.

An application of linear elasticity theory in II yielded, to first order, $\varrho/\varrho_0 \equiv d_0/d = 1 + \alpha P$, equal to the above expression for λ with $m=1$ (and to its first order expansion for any m) and to equation (2.1.2) used in I if α and β are identified.

Since (2.1.5) exhibits dependence on density as well as field, it may be expected that there will be electrostrictive as well as compressive contributions to P. The analysis of II yields

$$P = (\varepsilon_1 E_1^2/8\pi)\,\{1 + [\partial(\ln\varepsilon_1)/\partial(\ln\lambda)]_q\} \tag{2.1.7}$$

$$\doteq \frac{(E_1^2/8\pi)\,[2\varepsilon_\infty - 1 + ah(E)]}{1 - 2\alpha(\varepsilon_\infty - 1)(E_1^2/8\pi)}, \tag{2.1.8}$$

where the second equation only follows when $n=m=1$ and $r=0$.

Figures 3 and 4 show the agreement obtained for two temperatures when the theory of II is fitted to Grahame's[26] data. In these figures, the curves for different concentrations were progressively shifted upward by 6 μF/cm² to allow clear distinction between them. The only significant disagreement between theory and experiment for all temperatures and concentrations occurs on the anodic side and possibly arises from a specific adsorption process in this region not included in the theory.

It is clear that although the introduction of a non-zero $\mathcal{E}_n$ has made the theoretical curves somewhat asymmetric and allowed better curve fitting for low anodic potentials, especially for low temperatures, its introduction is insufficient to explain the rapid anodic rise in C. Parsons[24] has suggested that this rise comes not from specific adsorption but from a much greater compressibility of the inner layer at positive than at negative electrode charges. This is explained as arising from a difference in the strength of hydration of cations and anions, but the suggestion runs into difficulty because of the large temperature coefficient of compressibility needed in the anodic polarization region. The great similarity between NaF curves and those of other, specifically adsorbed electrolytes also reduces the likelihood of correctness of this explanation.

Considerable attention has been given by the authors[3,4] and, approximately simultaneously, by Watts-Tobin[30] to the problem of explaining the relatively small value of $a \equiv \varepsilon_1^0 - \varepsilon_\infty$, the unsaturated dipole contribution to the dielectric constant in the inner layer. A common partial explanation involved the assumption that the field acting on the two-dimensional, inner-layer water molecules was essentially equal to the applied field. In the present work, more detailed consideration of this effective field leads, as we shall see, to the conclusion that the dipole reaction field partially cancels the applied field, rendering the effective field even smaller. Also, there is general agreement that the correlation between the instantaneous directions of neighboring dipoles is much reduced in a two-dimensional water layer from that in bulk water, and association may be further reduced because surface water molecules will settle down

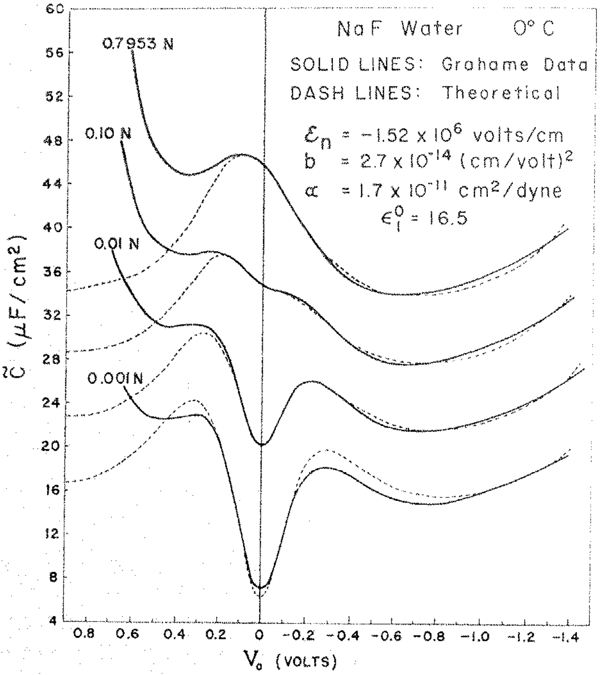

FIG. 3. Comparison of the results of the theory of II and Grahame's experimental differential capacitance results for 0°C.

somewhat between surface mercury atoms.[3,4,6] In addition, in II the effect on a and on the saturation parameter b of single and infinite imaging of surface dipoles was quantitatively evaluated and fair agreement with experiment found.

In fitting Grahame's curves in II, it was found that excellent agreement at all temperatures could be obtained by employing the theoretically expected temperature dependence of b, but that the temperature dependence of a obtained from fitting curves at five temperatures was very regular but was appreciably greater than that predicted by any theoretical model considered. Part of this discrepancy may arise from the neglect of molecular interaction in the plane, which would itself be temperature dependent (see later discussion). In spite of the disagreement in the temperature coefficient of a obtained by curve fitting, the general rather close agreement found in II between the values of a, b, and α and either theoretical or experimental values obtained in other ways is good evidence of the reality of the compression and saturation effects embodied in the theory.

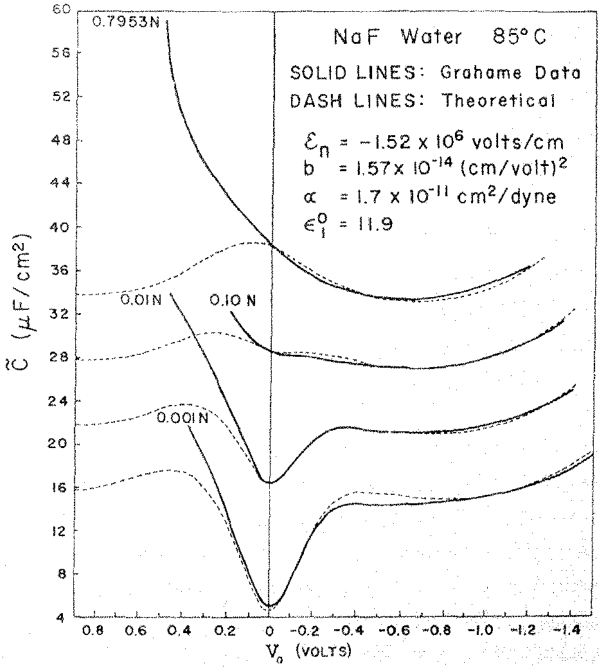

FIG. 4. Comparison of the results of the theory of II and Grahame's experimental differential capacitance results for 85°C.

The interesting hump which appears in Fig. 2 at low temperatures and in Fig. 3 near but slightly to the anodic side of the ecm was originally explained by Grahame[26] as arising from an increase in thickness of an ice-like layer next to the electrode as the temperature is lowered. The present authors[3,4] and Watts-Tobin[30] have alternatively suggested that it arises from the proportioning of two factors: an increase in capacitance arising from specific adsorption as anodic polarization is increased, and then an initial decrease as dielectric saturation begins. Mott and Watts-Tobin[6] in their further work have ignored the effect of the natural field $\mathcal{E}_n$ in shifting the hump to the anodic side of the ecm and have explained such a shift on the basis of a displacement between the zeros of charge and potential arising from specific adsorption; this explanation will be considered in the next section.

Next, let us compare different methods that have been used to introduce dipole orientation effects. We shall initially neglect the effect of density changes on the dielectric constant and consider the potential difference, V_1, across the inner layer only. In II, we took

$$V_1 = 4\pi qd/\varepsilon_1, \tag{2.1.9}$$

$$\begin{aligned}\varepsilon_1 &= \varepsilon_\infty + [4\pi N_v <\mu(E)>/E] \\ &\equiv \varepsilon_\infty + ah(E),\end{aligned} \tag{2.1.10}$$

where $<\mu(E)>$ is the average value of the permanent dipole moment in the direction of the field E, $E \equiv E_1 + \mathcal{E}_n$ as before, and N_v is the number of dipoles per unit volume. Their number per unit area in an adsorbed monolayer will be denoted by N (not to be confused with the normality of the solution). If we temporarily assume $|\mathcal{E}_n| \ll |E_1|$, write $N_v d \equiv N$, and use $E_1 = V_1/d$, it can be readily shown that (2.1.9) and (2.1.10) lead to

$$V_1 \cong \frac{4\pi qd}{\varepsilon_\infty} - \frac{4\pi N <\mu(E)>}{\varepsilon_\infty}, \tag{2.1.11}$$

consistent with $D = \varepsilon_1 E_1 = 4\pi q$. The approximate equality is exac when $\mathcal{E}_n = 0$.

In the present notation, Watts-Tobin[30] and Mott and Watts-Tobin have esentially written

$$V_1 = \frac{4\pi qd}{\varepsilon_\infty} - \frac{4\pi N <\mu(E)>}{\varepsilon_\infty}, \tag{2.1.12}$$

which is exactly the same as (2.1.11) when $\mathcal{E}_n = 0$. On the other hand, when $\mathcal{E}_n \neq 0$, equations (2.1.9), (2.1.10), and (2.1.12) are not entirely consistent. We are now of the opinion that the formulation of (2.1.12) is the more nearly correct; however, because $|\mathcal{E}_n| \ll |E_1|$ over most of the range of E_1, the difference between the two approaches would have an almost negligible effect on the curve fitting of II.

Let us now consider how (2.1.12) may be derived and then improved. Following Mott and Watts-Tobin, in a layer containing dipoles we shall give up the definition $\varepsilon_1 \equiv D/E_1$. Instead, we may write

$$D \equiv 4\pi q = E_1 + 4\pi(\mathcal{P}_1 + \mathcal{P}_2), \tag{2.1.13}$$

$$\mathcal{P}_1 \equiv (\varepsilon_\infty - 1)E_1/4\pi, \tag{2.1.14}$$

$$\mathcal{P}_2 \equiv N_v \langle \mu(E) \rangle. \tag{2.1.15}$$

Solving for the potential drop $V_1 \equiv E_1 d$ yields just (2.1.12). Note that when $q=0$, $E_1 \equiv E_{10}$ is non-zero and is given by

$$E_{10} = -\frac{4\pi N_v \langle \mu(E_{10} + \mathcal{E}_n) \rangle}{\varepsilon_\infty}, \tag{2.1.16}$$

which must be solved by iteration when $\mathcal{E}_n \neq 0$ and $E_{10} \neq 0$. When $\mathcal{E}_n < 0$, $E_{10} > 0$ and q will therefore be positive when $E = 0$, the point of no average dipole orientation where the hump may be expected to be most prominent.

We believe that (2.1.12) and (2.1.16) still require considerable further modifications which, for greater clarity, we shall introduce bit by bit. The changes chiefly concern the proper inclusion of electronic and distortional polarization and planar interactions. In the preceding treatment, these polarizations were introduced through the ε_∞, or $\mathcal{P}_1$ term. Although the technique for handling this polarization is proper for bulk, we believe that for the present case of a monolayer a more nearly correct treatment should be based upon the actual monolayer structure.

Equations (2.1.13) and (2.1.15) require no modification if E is properly defined; we must, however, determine the proper dependence of $\mathcal{P}_1$ which will take the place of (2.1.14). For bulk one has the relations

$$\mathcal{P}_1 = \alpha_1 \mathcal{E}_{\text{eff}}, \tag{2.1.17}$$

$$\mathcal{E}_{\text{eff}} = E_1 + (4\pi \mathcal{P}_1/3), \tag{2.1.18}$$

$$D = \varepsilon_\infty E_1 = E_1 + 4\pi \mathcal{P}_1. \tag{2.1.19}$$

connecting the microwave volume polarizability α_1 with ε_∞. Combining these equations leads to the usual result, $\alpha_1 = 3(\varepsilon_\infty - 1)/4\pi(\varepsilon_\infty + 2)$, evaluated for bulk material. The polarizability constant α_1 will be the same for the monolayer as for bulk except for a correction arising from differences in the density and for possible covalent bonding effects which we shall ignore. On taking $\varrho_0' \equiv$ density in the bulk at zero electrostatic pressure and defining $\chi_0 \equiv \varrho_0/\varrho_0'$, we have that $\lambda\chi_0 = (\varrho/\varrho_0)(\varrho_0/\varrho_0')$ $= \varrho/\varrho_0$, a quantity of the order of unity. Inclusion of this factor leads to the following relation for α_1 in the monolayer,

$$\alpha_1 = \lambda\chi_0 [3(\varepsilon_\infty - 1)/4\pi(\varepsilon_\infty + 2)] \equiv \lambda\alpha_{10}. \tag{2.1.20}$$

Under the very high fields which may prevail in the inner region, α_{10} may show some saturation behavior and may decrease with increasing field magnitude. This effect should be relatively small and will not be further considered.

We shall now briefly set aside macroscopic electrostatics and determine the polarization and local electric fields from microscopic laws, neglecting discreteness of charge in the electrode itself.[40a] Having then found the total polarization, we may determine the macroscopic electric field acting in the inner layer through relation (2.1.13) with $\mathcal{P} \equiv \mathcal{P}_1 + \mathcal{P}_2$, the total polarization.

In the monolayer, we still have $\mathcal{P}_1 = \alpha_1 \mathcal{E}_{\text{eff}}$ with α_1 given by (2.1.20), but now $\mathcal{E}_{\text{eff}}$ no longer follows from (2.1.18). Instead, we find that $\mathcal{E}_{\text{eff}}$ is made up of the applied field $4\pi q$ plus the fields arising from the permanent dipole moment, and from electronic and distortional polarizations. Under some conditions, which will be explored elsewhere, it will be desirable to introduce a new natural field, different from the orienting field $\mathcal{E}_n$, which induces polarization even when q and $<\mu>$ are zero. This natural field will be taken zero here, but its introduction will usually lead to better agreement between theory and experiment and may be further justified on the basis of the likely presence of a strong inhomogeneous field at the surface of a clean metal. Defining r_0 as the separation of atoms in the hexagonally arranged monolayer, we have that $r_0^{-3} = (3/4)^{3/4} N^{3/2}$. Ignoring effects of correlations between the instantaneous orientations of different dipoles, we shall determine the field orienting the dipoles and polarizing the electrons in a self-consistent way by replacing all dipole moments by their statistical time averages and requiring that the resulting orienting field indeed produces such average polarization. Here we shall make use of the fact that the field perpendicular to the plane at the position of a dipole in a hexagonal array of normally oriented dipoles, produced by all the other dipoles in the array, is given by $-r_0^{-3}\sigma$ times the dipole moment per dipole. The quantity σ represents a geometrical factor which for a hexagonal array of ideal dipoles equals[41] 11·034; for a square array its value is 9·0336. For non-ideal dipoles, such as those of water molecules, these factors will be somewhat reduced.[42]

The above procedure leads to the result that the effective field acting to create distortional and electronic polarization is

$$\mathscr{E}_{\mathrm{eff}} = 4\pi q-(3/4)^{3/4}\sigma N^{3/2}[<\mu> +(\mathscr{P}_1/N_v)], \tag{2.1.21}$$

where $<\mu> \equiv <\mu(\mathscr{E})>$, and $\mathscr{E}$ is an orienting field determined later. This result together with (2.1.17) yields

$$\mathscr{P}_1 = [4\pi q\lambda\alpha_{10}-s\lambda N^{3/2}<\mu>]/\varepsilon_{\mathrm{eff}}, \tag{2.1.22}$$

where $s \equiv (3/4)^{3/4}\,\sigma\,\alpha_{10}$ and $\varepsilon_{\mathrm{eff}} \equiv 1+sd_0N^{1/2}$. In deriving (2.1.22), we have made use of the monolayer relations $N_v = N/d = N\lambda/d_0$; and we have tacitly derived the polarizability parameter α_{10} from the properties of the monolayer substance alone, ignoring the point that contributions from electrode atoms and diffuse layer ions may result in a slightly altered value of the average inner-layer polarizability. The effective dielectric constant, $\varepsilon_{\mathrm{eff}}$, derived here from microscopic considerations, will usually range from unity to two or three in magnitude. Combining equations (2.1.21) and (2.1.22) leads to

$$\mathscr{E}_{\mathrm{eff}} = [4\pi q-(3/4)^{3/4}\sigma N^{3/2}<\mu>]/\varepsilon_{\mathrm{eff}}. \tag{2.1.23}$$

The present expression for $\varepsilon_{\mathrm{eff}}$ applies in the case of maximum surface coverage by a monolayer of dipolar molecules. For variable coverage, a form of this expression was first derived by Roberts.[43–45] In the maximum coverage case, his result reduces to the present $\varepsilon_{\mathrm{eff}}$ except for the replacement of the term $(3/4)^{3/4}\times 11{\cdot}034 \cong 8{\cdot}894$ by $1\times 9{\cdot}034 \cong 9$, a change appropriate for a square array. The near equality of these numbers shows that the magnitude of $\varepsilon_{\mathrm{eff}}$ is virtually independent of which type of array is assumed. The present treatment seems to be the first for which $\varepsilon_{\mathrm{eff}}$ has been introduced in a self-consistent treatment with $q\neq 0$ and $<\mu> \neq \mu_0$, where μ_0 is the magnitude of the permanent dipole moment when $q=0$ and $\varrho=\varrho_0$.

Now we turn to the problem of calculating $<\mu>$. In this task we shall be guided by the methods just employed to find $\mathscr{P}_1$. In particular, we must consider in some detail the overall effective field orienting the permanent dipoles. We have already taken into account all such orienting effects independent of q by the introduction of the natural field $\mathscr{E}_n$. The assumptions of independence and additivity of $\mathscr{E}_n$ and the extra field present when $q\neq 0$ are probably good under most conditions, especially if $\mathscr{E}_n$ is found to have little or no temperature dependence. The orienting field arising from q was taken as $E_1 = 4\pi q/\varepsilon_1$ in I and II and as V_1/d, with V_1 given by (2.1.12), by Watts-Tobin[30] and Mott and Watts-Tobin.[6] As we have seen, these choices are not usually very different, but they share the defect of treating the field arising from dipole orientation in a manner appropriate only to bulk calculations.

If one removes a single dipolar molecule from the hexagonal sheet but leaves all other charges fixed as they were, the true field at the vacancy would, by the foregoing development, be just $\mathcal{E} = \mathcal{E}_{\text{eff}}$. With the missing molecule returned to its site, the effective field acting on the permanent dipole will be altered by the electronic polarization of that same molecule, and this effect will generally depend on the specific orientation of the molecule in a complicated and uncertain manner. Such dependence upon orientation of the shielding of the permanent dipole moment by the electronic polarization could actually affect the saturation function in a drastic and asymmetrical manner, depending on detailed molecular structure. In the present work, however, we shall neglect such asymmetry and assume that the electronic polarization shields the dipole through a factor n^2, the square of the optical refractive index, appropriately modified for density changes. Such modification, along the lines of equation (2.1.5) with the parameter $n=1$, leads to the replacement of n^2 by $1+\lambda(n^2-1)$. (We then finally obtain the following result for the total orienting field

$$\mathcal{E} = \mathcal{E}_n + [\mathcal{E}_{\text{eff}}/\{1+\lambda(n^2-1)\}]. \tag{2.1.24}$$

Next, we need to calculate the pressure in the inner region in the present regime. Since ε_1 has not been defined in the present treatment of a surface dipole layer, equation (2.1.7) relating pressure, ε_1, and E_1 cannot be used here to yield the pressure P. Employing the same general approach as that used in II (but see the statement after Ref. 4 for minor corrections), we obtain the following generalization of (2.1.7),

$$\begin{aligned} P &= \frac{qE_1}{2} + 2\pi\lambda q\left(\frac{\partial\mathcal{P}}{\partial\lambda}\right)_q \\ &= 2\pi q\left[q - \mathcal{P} + \lambda\left(\frac{\partial\mathcal{P}}{\partial\lambda}\right)_q\right], \end{aligned} \tag{2.1.25}$$

on using (2.1.13). The total polarization $\mathcal{P}$ follows immediately from (2.1.15) and (2.1.22) and is

$$\mathcal{P} = [4\pi q\lambda\alpha_{10} + (\lambda N/d_0)\langle\mu\rangle]/\varepsilon_{\text{eff}}. \tag{2.1.26}$$

Let us now write $\langle\mu(\mathcal{E})\rangle \equiv \lambda^{-1}\mu_0 f(\mathcal{E})$, where the factor λ^{-1} is introduced to account, to first order, for molecular compression in the inner region and consequent reduction of the magnitude of the permanent dipole moment (see II). The saturation function $f(\mathcal{E})$ obeys $f(0)=0$, $f(\infty)=1$. Note that the usual assumption of $r=0$ in (2.1.5) is equivalent to taking $N_v<\mu> = N\mu_0 f(\mathcal{E})/d_0$ if $N_v=\lambda N/d_0$, in agreement with the λ^{-1} term introduced above. We may now express the pressure as

$$P = 2\pi q\left[q-\left(\frac{N\mu_0}{d_0\varepsilon_{\text{eff}}}\right)\left\{f(\mathcal{E})-\lambda\left(\frac{\partial f(\mathcal{E})}{\partial\lambda}\right)_q\right\}\right], \qquad (2.1.27)$$

where terms in $\mathcal{D}$ and $\partial\mathcal{D}/\partial\lambda$ involving the polarizability α_{10} have cancelled out.

The mean field in the inner region now follows from (2.1.13) and (2.1.26) and is

$$E_1 = 4\pi q\,[1-\lambda(4\pi\alpha_{10}/\varepsilon_{\text{eff}})]-[4\pi N\mu_0 f(\mathcal{E})/d_0\varepsilon_{\text{eff}}]. \qquad (2.1.28)$$

Note that at $q=0$ the expression for E_{10} does not involve E_{10} itself in $\mathcal{E}$, as is the case for (2.1.16). The potential drop $V_1=E_1 d=E_1\lambda^{-1}d_0$ is

$$V_1 = 4\pi q\lambda^{-1}d_0\,[1-\lambda(4\pi\alpha_{10}/\varepsilon_{\text{eff}})]-[4\pi N\mu_0 f(\mathcal{E})/\lambda\varepsilon_{\text{eff}}], \qquad (2.1.29)$$

which may be compared with (2.1.12).

When this result is compared with (2.1.12) suitably modified to include density dependence, one sees that the term $\{1-\lambda(4\pi\alpha_{10}/\varepsilon_{\text{eff}})\}^{-1}$ replaces the simpler $\{1+\lambda(\varepsilon_\infty-1)\}$. Since the terms multiplying λ are not small compared to unity, the λ dependence of these two expressions will be considerably different. Secondly, comparison of the second terms shows that $\lambda\,\{1+\lambda(\varepsilon_\infty-1)\}$ is replaced by $(\lambda\,\varepsilon_{\text{eff}})$ if the appreciable difference between E and $\mathcal{E}$ is ignored.

The potential drop across a dipole layer measured at points a large distance on either side of the layer is frequently written as $4\pi N<\mu>$. When the dipoles are non-ideal and the dipole layer can be approximated by two continuous charge layers with homogeneous material of ε_∞ between them, the result of equation (2.1.12) follows, $4\pi N<\mu>/\varepsilon_\infty$. Ignoring the differences between λ and unity, one sees that the present result, which includes planar interaction of ideal dipoles in a layer, is of the same general form, if not magnitude, as these expressions. It will remain essentially the same when the dipoles are only approximately ideal,[42] and we believe that it is pertinent not only to double-layer calculations under close-packed conditions but also to the problem of the potential difference produced by a layer of molecules having permanent dipole moments adsorbed from a gas phase in a regular but not necessarily close-packed array on a surface.[40a]

Finally, to obtain V_0, the total p.d. across the double layer, we must include V_2, that across the diffuse region. However, since it is customary and desirable to measure potential in an unabsorbed system with reference to the ecm potential ($q=0$), we must also subtract $V_{10} \equiv E_{10}d_0$, to obtain

$$V_0 = 4\pi q\lambda^{-1}d_0\,[1-\lambda(4\pi\alpha_{10}/\varepsilon_{\mathrm{eff}})]+(2kT/e)\sinh^{-1}(q/2A) \\ -(4\pi N\mu_0/\varepsilon_{\mathrm{eff}})\,[\lambda^{-1}f(\mathcal{E})-f(\mathcal{E}_0)], \qquad (2.1.30)$$

where $\mathcal{E}_0$ is the value of $\mathcal{E}$ at $q=0$ and is zero when $\mathcal{E}_n=0$. Since $P=0$ when $q=0$, $\lambda \equiv (1+m\alpha P)^{1/m}$ will be unity at this point. The above expression shows all λ-dependence explicitly except that in $f(\mathcal{E})$. It is expected that the hump will appear at low temperatures in the neighborhood of the q value for which $\mathcal{E}=0$. This will occur at a positive q for $\mathcal{E}_n<0$.

For $f(\mathcal{E})$ we shall follow Grahame[35] and II in using an expression of the form $f(\mathcal{E}) = (2/\pi)\tan^{-1}(\sqrt{[b]}\mathcal{E})$. This form has the advantage discussed in II of being able to approximate either Langevin or dipole-image saturation behavior by adjustment of the parameter b. Both Langevin and dipole-image saturation are based on the assumption that dipoles are free to point in any direction. On the other hand, Watts-Tobin[30] and Mott and Watts-Tobin[6] assumed that a water dipole could only take up two positions, leading to $f(E)=\theta\tanh(\theta\mu_0E/kT)$, where $\theta=1/\sqrt{3}$ in Watts-Tobin's detailed treatment of the water molecule, and $\theta=1$ when it was assumed[6] that the dipole could only be parallel or antiparallel to E. By selection of b, the $\tan^{-1}$ form may also be made to approximate to this result in the saturation region of most interest.

It was shown in II that $\sqrt{b}$ must be proportional to the magnitude of the dipole moment, say μ. But in both II and the present treatment we take $\mu=\lambda^{-1}\mu_0$ to account for dipole compression. Thus, $\sqrt{b}$ must be replaced by $\lambda^{-1}\sqrt{b}$ and $f(\mathcal{E})$ becomes

$$f(\mathcal{E}) = (2/\pi)\tan^{-1}[\lambda^{-1}\sqrt{(b)}\mathcal{E}\,], \qquad (2.1.31)$$

where $\sqrt{b}$ controls the sensitivity of the saturation effect and is now independent of λ. The λ^{-1} term was unfortunately omitted in the curve fitting carried out in II. Since λ there reached a maximum of only 1·1, the effect is small and could approximately be taken into account by a few per cent reduction in $\sqrt{b}$. It will be noted that $f(\mathcal{E})$ involves λ through the above λ^{-1} and through the term $[1+\lambda(n^2-1)]$ in $\mathcal{E}$. Since the form of the latter is uncertain anyway for reasons previously discussed, it seems reasonable to neglect its λ-dependence in obtaining $(\partial f/\partial\lambda)_q$ for (2.1.27).

The presence of $<\mu>$ or $f(\mathscr{E})$ in $\mathscr{E}$ itself shows that planar-interaction depolarization may have an important effect on the approach to saturation. The effect is to retard the achievement of saturation, and its presence makes the exact choice of $\tan^{-1}$, tanh, or Langevin saturation expressions both less certain and less important. In II the situation was examined where water dipoles were imaged in the electrode or in the electrode and the diffuse layer. Single imaging produced little deviation from Langevin saturation but deviation was somewhat more pronounced in the case of an infinite series of images. Such imaging leads to a more rapid approach to saturation, opposite to the effect of planar depolarization. Thus far, no treatment has been given in which planar depolarization and dipole imaging have been simultaneously considered. Because the effect of single imaging is small and there is some doubt concerning the appropriateness of infinite imaging (see later discussion), we believe that for the present it is most reasonable to use the interpolation formula (2.1.31) with b adjustable to describe saturation behavior.

Preliminary results of fitting the present theory to Grahame's NaF data indicate that a reasonable fit to $\tilde{C}$ curves may be achieved over almost the entire experimental V_0 span, anodic as well as cathodic. Such agreement is produced without the need to invoke specific adsorption processes and indicates that the hump on the anodic side arises from an $\mathscr{E}_n<0$ and from the presence of induced and permanent dipole moments which depend quite differently on q. These results will be discussed at length elsewhere.

2.2. *Specific Ionic Adsorption*

Let us now suppose that a charge q_1 (per unit area) arises from specifically adsorbed ions. It will usually be assumed that these ions are solely anions. Since the actual dependence of q_1 on q or V_0 involves discreteness of charge effects, such dependence will be discussed later.

It is important to point out that the differential capacitances of the inner and diffuse layers are no longer exactly in series when $q_1 \neq 0$. Charge neutrality requires that $q=-(q_1+q_2)$, where q_2 is the total diffuse region charge. To the degree to which an OHP can be well defined, it is proper to write $V_0 = V_1+V_2$ with the zero of V_0 selected so that $V_0=0$ when $q=0$ for the case of no specific adsorption of ions. Differentiation now yields

$$\frac{dV_0}{dq}=\frac{dV_1}{dq}+\left(\frac{dV_2}{dq_2}\right)\left(\frac{dq_2}{dq}\right), \tag{2.2.1}$$

or

$$\tilde{C}^{-1} = \tilde{C}_1^{-1} - \left(\frac{\mathrm{d}q_2}{\mathrm{d}q}\right)\tilde{C}_2^{-1} = \tilde{C}_1^{-1} + \left(1 + \frac{\mathrm{d}q_1}{\mathrm{d}q}\right)\tilde{C}_2^{-1}. \qquad (2.2.2)$$

Since $\mathrm{d}q_2/\mathrm{d}q$ may be positive when $q_1 \neq 0$, the possibility exists that $\tilde{C}$ may greatly exceed $\tilde{C}_1$; this possibility is, however, usually experimentally unimportant since $|\mathrm{d}q_2/\mathrm{d}q|$ is almost always found to be less than unity. It should also be mentioned that specific adsorption can, of course, cause a direct increase in $\tilde{C}_1$ itself compared to that without such adsorption. Grahame[46] was the first to point out qualitatively that in the presence of specific adsorption large capacitance values arise because of the change of adsorption with potential. An equation fully equivalent to (2.2.2) was given in II, and a similar, less general, equation was derived by Devanathan,[29] to whom belongs the credit for first showing in detail the failure of the series assumption when $q_1 \neq 0$. Many authors have treated the double layer with the simplifying approximation of neglecting the potential drop across and capacitance of the diffuse region. Clearly, this will be a very poor approximation when $(\mathrm{d}q_2/\mathrm{d}q)\ \tilde{C}_2^{-1}$ is comparable in magnitude with $\tilde{C}_1^{-1}$. Further, in this case it may not even be a very good approximation to use ordinary simple diffuse layer theory for $\tilde{C}_2$.

Three different methods of calculating ionic surface charge excesses at the mercury–solution interface are presently available. These are the electrocapillary method,[20] which requires a graphical differentiation of the interfacial tension; Grahame's[20,47] capacity method, which requires both a differentiation and a double integration; and the non-thermodynamic double-layer model method pioneered by Devanathan.[29] Since these methods have recently been discussed and compared by Devanathan and Canagaratna,[48] we shall here consider only the third.

Figure 5 is a conventional diagram for the diffuse layer in the presence of specific adsorption showing the thicknesses β and γ, dielectric constants, p.d.'s, and charges. Because of the smearing out of charge, all p.d.'s shown are average values, thus V_i is the *mean* p.d. between the bulk of the solution and the IHP. There are, however, conceptual difficulties associated with this continuously distributed charge model which we shall discuss before outlining its usual treatment and some generalization thereof. Let q_{1m} be the saturated value of q_1 appropriate when all surface sites on the metal are occupied by specifically adsorbed ions (to be denoted by SAI, taken plural or singular) and no water molecules are left in the inner region. Further, let $\theta \equiv q_1/q_{1m}$ denote the fractional occupation of the surface by specifically adsorbed ions.

Now when $\theta \ll 1$, at any given time there will be appreciable surface regions where there will be no SAI nearby and the surface will be occupied as usual by water molecules in the inner layer. For these regions, it is proper to take $\beta+\gamma \equiv d$, $\varepsilon_\beta = \varepsilon_\gamma \equiv \varepsilon_1$, and essentially ignore SAI when calculating V_1. Although the introduction of an ε_1 which includes dipole orientation effects is not the best procedure, as we have seen in the last Section, ε_1 will be used here as a shorthand way of referring to and including dipole orientation effects. On the other hand, in the neighborhood of a SAI, the thickness β will be made up of a contribution from the metal and one from the radius of the SAI, and clearly ε_β will involve no polar contribution and will generally differ appreciably from ε_1. Also, it is reasonable to suppose that a SAI will retain its first hydration shell on the side away from the surface so that the center of charge of the nearest diffuse-layer (hydrated) ion will be separated from that of the SAI by approximately two ionic radii (usually radii of an anion and a cation) and the diameter of a water molecule. In such regions, γ will approximately equal the above d, ε_γ will approximately equal the ε_1 appropriate at the field in this region, and $\beta+\gamma$ will appreciably exceed d. Thus, in the neighborhood of SAI, the distance to the OHP will be greater

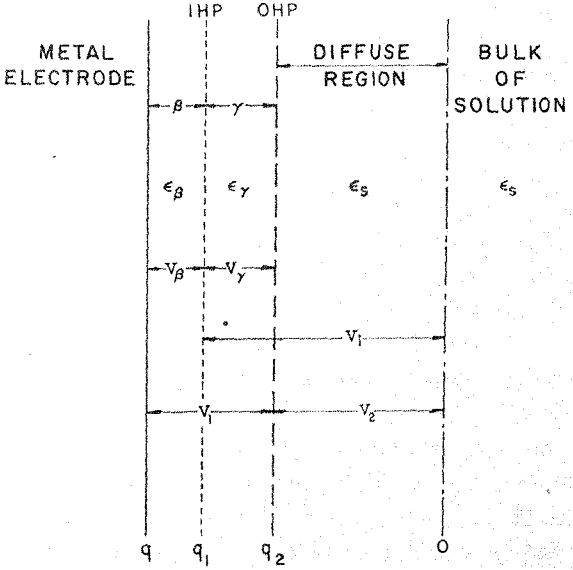

FIG. 5. Quantities defined in the double layer when discreteness-of-charge effects are ignored.

than that in a region where there are no SAI nearby and the OHP will not really be a plane.

In the conventional model of Fig. 5, the use of β, γ, ε_β, and ε_γ represents an averaging over the above situation, necessitated by the use of continuous charge distributions. Unfortunately, such averaging, which may be partly justified physically by thermal motion parallel to the electrode, will clearly be a function of θ and is one reason why $\gamma/(\beta+\gamma)$ is usually found to depend on q (and so on q_1) even without the introduction of compression effects.

The usual treatment of the diffuse layer yields

$$V_2 = -(2kT/e)\sinh^{-1}(q_2/2A), \tag{2.2.3}$$

and electrostatic theory leads to

$$V_\beta = 4\pi q\beta/\varepsilon_\beta, \tag{2.2.4}$$

$$V_\gamma = 4\pi\gamma(q+q_1)/\varepsilon_\gamma. \tag{2.2.5}$$

The use of $V_0 \equiv V_\beta + V_\gamma + V_2$ and rearrangement gives

$$V_0 = \left(\frac{2kT}{e}\right)\sinh^{-1}\,[(q_1+q)/2A] + 4\pi q\left[\frac{\beta}{\varepsilon_\beta} + \frac{\gamma}{\varepsilon_\gamma}\right] + \frac{4\pi q_1\gamma}{\varepsilon_\gamma}. \tag{2.2.6}$$

No direct dipole orientation potential contribution has been included in (2. 2. 6) but it is included in an approximate way, as shown previously, if ε_γ is not taken completely saturated. This is somewhat the course taken by Levine, Bell, and Calvert,[49] who also take $\varepsilon_\beta = \varepsilon_\gamma = \varepsilon_1 = \varepsilon_1^0$, of magnitude 10–20, but ignore dipolar saturation effects. Note that in Equations (2.1.1), (2.1.30), and (2.2.6) the simple addition of the diffuse region p.d., V_2, is only valid under the present approximation of smeared or continuous charge distributions, an approximation which will improve as the concentration of charge in the diffuse layer nearest the electrode increases.

If ε_β and ε_γ are both taken equal to ε_∞, it is not clear how to take the direct dipole contributions to V_0 into account. It was neglected (or taken constant) by Devanathan,[29] who was the first to give Equation (2.2.6) with $\varepsilon_\beta = \varepsilon_\gamma = \varepsilon_\infty$ (=7·19), $\beta+\gamma = 3{\cdot}72$Å, and β taken as the crystallographic radius of the adsorbed ion. One reason for the difficulty in properly accounting for this contribution in the present model is that there are probably two types of water dipoles concerned whose proportions change with θ: namely, those next to the mercury away from SAI, and those between SAI and the nearest diffuse layer ions. Furthermore, the presence of adsorbed ions in the inner region changes the planar interaction effect which resulted in the introduction of ε_{eff} in the last Section. This problem will be further considered later.

Grahame[28,50] and Grahame and Parsons[9] have used an equation equivalent to (2.2.6) with $\varepsilon_\beta = \varepsilon_\gamma = \varepsilon_\infty$ and no separate dipole orientation contribution. If the second term on the right is termed ψ^{02} and the last ψ^v following these authors, then $(q\psi_v/q_1\psi_{02}) = \gamma/(\beta+\gamma)$, but this is a dubious equation for all the reasons discussed above. In an early treatment, Grahame[50] did distinguish between the dielectric constant ε_γ in ψ^v and that in ψ^{02} when ε_β is taken equal to ε_γ there, but this is clearly not a meaningful distinction and can only be introduced heuristically in an effort to correct for deficiencies in the equation.

Mott and Watts-Tobin[6] have also given an equation equivalent to (2.2.6) when V_2 is omitted and $\varepsilon_\beta = \varepsilon_\gamma = \varepsilon_\infty$ $(=3)$ is used. No direct dipole orientation term was included although, as discussed previously, this term did appear in their treatment when specific adsorption was omitted.* They give as the condition that the field in the inner region be zero, $q(\beta+\gamma) = -q_1\gamma$, or $q = (\gamma/\beta)q_2$. This condition makes $V_1 \equiv V_\beta + V_\gamma = 0$ (when $\varepsilon_\beta = \varepsilon_\gamma$) but does not require a zero average field in the inner region; instead, it only leads to $\beta E_\beta = -\gamma E_\gamma$, where E_β and E_γ are the mean fields in the β and γ regions of the inner layer. There is thus no reason to expect, as do Mott and Watts-Tobin, that the hump on the anodic side should occur just at this charge. The data of Grahame and Parsons on KCl, in fact, do not substantiate the above relation between q and q_1 at the hump unless $\gamma/(\beta+\gamma)$ is taken to decrease very rapidly with increasing KCl concentration (or decreasing q). In general, we believe the hump will appear in the neighborhood of the electrode charge for which there is zero average dipolar orientation. Ignoring rapid fluctuation effects, we note that this is the charge for which the average dipole orienting field, $\mathscr{E}$ in Section 2.1, is zero. This will, in general, not be the condition which makes the mean fields E_β and/or E_γ zero or the condition which makes the potential zero at the position of an adsorbed ion (the micropotential — see Section 3).

Grahame and Parsons[9] have also taken the field in the inner region zero when $V_1=0$ and are concerned that V_2 is not also zero at this point. Although they indicate that this is a defect in the model which may partly explain the appearance of appreciable dependence of $\gamma/(\beta+\gamma)$ on q, this is not really the case. The model, in fact, leads to continuity of the mean

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* A less accurate combination of dipole orientation and specific adsorption terms was, however, given earlier by Watts-Tobin.[39]

electric displacement across the OHP, as is required by macroscopic electrostatics. At $V_1=0$, $V_2\neq 0$ since $E_\gamma \neq 0$. It is only when the picture is used of a linear mean potential variation across the inner region even in the presence of SAI that difficulties arise. The basic difficulty, as discussed earlier, arises from the use of the continuously distributed charge model of Fig. 5 at all when $\theta > 0$.

Devanathan[29] pointed out that (2.2.6) can give the shift of ecm potential with solute concentration provided q_1 at $q=0$ is known. One must only calculate V_0 vs. q_1 at $q=0$. The resulting curve will be correct, of course, to the degree to which (2.2.6) is an adequate description of the true situation in the double layer. For reasons already mentioned, we believe that (2.2.6) is only a poor representation of the true state of affairs, either with $\varepsilon_\beta = \varepsilon_\gamma = \varepsilon_\infty$ or even with $\varepsilon_\beta \neq \varepsilon_\gamma$ and ε_γ including a dipole orientation contribution which is saturable.

Grahame[28] and Grahame and Parsons[9] are not concerned with using (2.2.6) to obtain $\tilde{C}$ by differentiation and either the derivation therefrom of q_1 vs. q assuming values for $(\beta+\gamma)/\varepsilon_\infty$ and $\gamma/\varepsilon_\gamma$ or vice versa. Instead, they calculate q_1 vs. q using Grahame's capacity method, derive V_1 from KI and KCl differential capacitance data and plot V_1 vs. q_1. This procedure surprisingly shows that $(\beta+\gamma)/\varepsilon_\infty$ and $\gamma/\varepsilon_\infty$ are nearly independent of q over a wide range. Devanathan and Canagaratna[48] have, however, called the accuracy of Grahame's capacity method into question on the basis of a comparison of its predictions of surface excesses with those of the electrocapillary method. Nevertheless, the approximate constancy of the coefficients of q and q_1 in (2.2.6) is suggestive.

Levine, Bell and Calvert[49] have used (2.2.6) in conjunction with a theoretical relation between q_1 and electrode polarization, to be discussed later, to test these relations by calculating V_2 vs. V_0 and comparing with the results of Grahame's capacity method for KI. Quite good agreement is obtained, but the comparison of derived quantities is hazardous, and a much more stringent test would involve the direct calculation of $\tilde{C}$ vs. V_0 for several concentrations and temperatures.

Finally, Devanathan, in his early[29] and later[48] work with (2.2.6), has used it to calculate q_1, assuming that β, γ, and ε_∞ are known constants. A direct way of carrying out such a calculation would be first to obtain q vs. V_0 by integrating the experimental $\tilde{C}-V_0$ curve in the conventional way, then to calculate q_1 from (2.2.6) for given V_0 and q by iteration. Devanathan has used a more complicated but entirely equivalent method. On differentiating (2.2.6) with respect to q and keeping β, γ, and ε_∞ constant, he obtains an equation relating $(\mathrm{d}q_1/\mathrm{d}q)$ and $\tilde{C}$. This is essentially converted to an integral equation for q_1 which is then solved by iteration. Since no more information except for a constant of integration is used in this method than in the direct method, they must lead to identical results for q_1 vs. q if the zero of V_0 is picked consistent with the integration constant mentioned. Devanathan has not realized this fact and has substituted his q_1 values into (2.2.6) as a test of the theory. The resulting V_0 values are compared, at equal q's, with the experimental p.d. across the double layer. The resulting V_0 's are found to differ from the corresponding experimental p.d.'s by only a constant. This result is taken to be a stringent test of the theory; it is actually only a guarantee of the accuracy of the calculations. It is therefore not surprising that Devanathan's calculations of the shift of KCl ecm potential with concentration are in agreement with experiment; they must be, since they are calculated with q_1 values derived from the same data and nothing more.

It is worth pointing out that the q_1 values derived from (2.2.6) by the direct or by Devanathan's method using experimental $\tilde{C}$ values are only as correct as is (2.2.6) itself. In addition to the defects already mentioned, we should expect ε_γ and γ to vary with field because of compression effects. Therefore, it is surprising that surface excess values derived by Devanathan's method are frequently found to be in fairly reasonable agreement with values found by the electrocapillary method.[48] In fact, q_1 results derived from (2.2.6) with constant coefficients often seem much better than we might expect. On the other hand, the application of this method for cathodic polarization seems to lead to small cationic adsorption at strong cathodic charges. The presence of ionic adsorption on the cathodic side of the ecm is an alternative and much less satisfactory explanation of the shape of $\tilde{C}$ curves than that which assumes no adsorption but the presence of dielectric saturation and compression effects. This is especially so because for q more negative than about $-10\ \mu C/cm^2$ the specific adsorption found is independent of anion type and of concentration.[29] Further, specific adsorption should be quite strongly temperature dependent, but the shape of $\tilde{C}$ curves for $q < -10\ \mu C/cm^2$ is very nearly temperature independent. It is unfortunate that there is no $\tilde{C}$ vs. q data available for which one can be certain that there is no specific adsorption over a wide q range.

2.3. *Adsorption of Neutral Substances*

Two quite different types of differential-capacitance behavior have been observed for electrolytic solutions containing neutral substances. Thiourea,[51] for example, leads to results very similar to those found for the specific adsorption of simple ions. At constant thiourea concentration, double-layer differential capacitance increases rapidly on anodic polarization. On the other hand, aliphatic molecules seem to reach maximum adsorption at the interface in the region of the ecm, and capacitance curves approach that of the pure solution at strong anodic or cathodic polarization.[52]

A number of different approaches have been made to the problem of explaining the above behaviors. Since some of the earlier work has recently been considered by Bockris, Müller, and Devanathan,[53] we shall limit the present discussion to some of the recent work in the field. Let the number of neutral entities adsorbed per unit area be Γ (exclusive of water molecules in the inner layer), and define $\delta \equiv \Gamma/\Gamma_m$, the fractional surface coverage.* Here Γ_m is the number per unit area when the surface is entirely covered with the neutral substance. Further, let the p.d. V_0 across the double layer in the absence of neutral-substance adsorption ($\delta = 0$, but θ not necessarily zero) be now denoted as $V_0'(q)$. Devanathan[54] now assumes that when $\delta \geq 0$, the new double-layer p.d. will be

$$V_0(q) = V_0'(q) + \frac{2\pi\Gamma\mu_p}{\varepsilon_\infty}, \tag{2.3.1}$$

where μ_p is the permanent dipole moment of the adsorbed molecule, and ε_∞ is again the constant (saturated) value of the dielectric constant of water in the inner region, taken as 7·19. In order to take account of the direction of the dipole, Devanathan rewrote the second term on the right as $e_0\Gamma/K_{\mathrm{org}}$, where $K_{\mathrm{org}} \equiv \varepsilon_\infty/2\pi l$, $\mu_p \equiv e_0 l$, and the charge e_0 is positive when the positive end of the dipole is next to the electrode.

Now molecules of the adsorbed neutral substance may still be somewhat free to rotate, just as in the water molecule in the inner region, and it is therefore necessary to replace μ_p by $<\mu_p(\mathscr{E}_p)>$, where $\mathscr{E}_p$ is the effective field tending to orient the permanent dipole. Its approximate calculation, considering planar interaction, will be outlined later. Although Devanathan has given an argument to justify the factor 2 in equation (2.3.1), we believe, in agreement with the discussion of the matter by Higuchi, Ree, and Eyring,[55] that for dipole layers the 2 should be replaced by the more usual 4 (see equation 2.1.11, which is some further justification). Making the above changes, changing the sign of the dipole term to agree with

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* This quantity or the corresponding ratio of surface excesses is called θ by most authors; we here require another symbol in order to keep separate the treatment of specific ionic adsorption ($\theta > 0$) and adsorption of neutral substances ($\delta > 0$). Note that when δ and θ are simultaneously non-zero, $0 \leq \theta + \delta \leq 1$.

usual practice, and replacing ε_∞ by a constant factor η we have,

$$V_0(q) = V_0'(q) - [4\pi\Gamma < \mu_p(\mathscr{E}_p) > /\eta]. \tag{2.3.2}$$

A somewhat improved analysis and some discussion of η, which arises from planar interaction and is more complicated than the previous ε_{eff}, will be presented later in the paper.

In order to use (2.3.1) to obtain $\Gamma(q)$ for different concentrations, Devanathan[54] has held μ_p constant and differentiated (2.3.1) with respect to q, obtaining a relation between the differential capacitances with and without neutral-substance adsorption and involving the term $\mathrm{d}\Gamma/\mathrm{d}q$. Finally, $\Gamma(q)$ is obtained by integration. Unlike the case of specific ionic adsorption, data are always available where there is no adsorption of the neutral substance considered and the above method makes use of them directly without the integral equation and solution by the method of successive approximations required in Devanathan's treatment of specific ionic adsorption.

A much simpler way of obtaining $\Gamma(q)$ than that of Devanathan is to use (2.3.1), or, preferably, (2.3.2) directly. Since q vs. V_0 and vs. V_0' may be obtained by integration of differential capacitance data, (2.3.2) may be immediately used to yield $(\Gamma/\eta) < \mu_p(\mathscr{E}_p) >$ vs. q for a given neutral-substance concentration. Note that only when there is good evidence to believe that $< \mu_p > = \pm\mu_p$ and μ_p and η are known will it be possible, however, to obtain $\Gamma(q)$ separately. Further, it is important to point out that Devanathan's differential method will only yield $\Gamma(q)$ when $< \mu_p > = \pm\mu_p$, independent of charge on the electrode. If the dipoles are not fully pinned, differentiation leads to a term additional to $\mathrm{d}\Gamma/\mathrm{d}q$, which must be included. On the other hand, the use of (2.3.2) leads to $\Gamma < \mu_p(\mathscr{E}_p) > /\eta$ directly, independent of the restrictive condition $< \mu_p > = \pm\mu_p$.

Unfortunately, (2.3.2) itself cannot be accepted as a very good equation for some of the same reasons as those cited in the discussion of equation (2.2.6). Equation (2.3.1) or (2.3.2) has inherent in it the assumption that the only effect of the adsorption of neutral substance is the change in the double-layer p.d. in the manner cited. Actually, however, each molecule of neutral substance adsorbed displaces one or more water molecules in the inner region. Such displacement changes the p.d. arising from partly oriented water dipoles, making the actual $V_0'(q)$ variably different from the $V_0'(q)$ appropriate when δ is identically zero. Further, the surroundings of an adsorbed molecule of neutral substance will, in general, be somewhat different from those of an inner-region water molecule, and planar interaction will play an important and more complicated role than in the case of water molecules only in the inner layer. Again, the difficulty arises from a too naive smearing out of the properties of the inner layer in the presence of two or more species.

Devanathan[54] has used (2.3.1) to calculate $\Gamma(q)$ from the data of Schapink, Oudeman, and Helle[51] on thiourea in NaF. These authors themselves integrated their differential capacitance results twice to obtain interfacial tension vs. charge for each thiourea concentration, then applied the usual electrocapillary method to obtain $\Gamma(q)$ by differentiation of the interfacial tension with respect to the chemical potential of the thiourea. Contrary to Devanathan's [56] statement, this is not a fully thermodynamic method (since the capacitance measurements were made at 1025 c/s), but it should be valid if there was no frequency dependence of the differential capacitance between zero frequency and 1025 c/s (Schapink *et al.* do not mention testing this condition). The accuracy of the results is limited, however, by the accuracy of the graphical differentiation, itself applied to a curve plotted with relatively wide spacing of points. Comparison of the result for $\Gamma(q)$ shows fair semi-quantitative agreement (not the "good agreement" mentioned by Devanathan[56]), with worst agreement at high concentration in the lower cathodic polarization region. Agreement is probably helped by the likelihood that the thiourea molecule is, in fact, chemisorbed with its dipole pinned essentially perpendicular to the surface and with its negative end (the S-atom end) next to the mercury. Such specific adsorption probably arises from covalent bonding,[54] an overlap of mercury electrons with the lone pair of the sulfur atom.[57]

Devanathan[56] has refined the above approach somewhat in order to analyze differential capacitance measurements on those kinds of neutral substances most adsorbed in the neighborhood of the ecm. It is assumed[53,56] that aliphatic molecules are adsorbed with their hydrocarbon end (essentially zero permanent dipole moment) toward the mercury and their polar group outside the inner region. The dipole moment that enters into (2.3.1) is then that arising from the replacement of (assumed) fully oriented water dipoles by structures without a permanent moment. Further modification is made by using in the differential capacitance a δ-dependent average of the dielectric constant appropriate for $\delta=0$ (water only in the inner layer) taken as 7·19 and that for $\delta=1$ (hydrocarbon groups only in the inner region) taken as 1·60. No correction for δ-dependent thickness change of the inner layer is made, no change of dipole orientation with electrode charge is included, and no compression and electrostriction effects in the inner layer are considered.

The above changes introduced by Devanathan act in the direction of increasing the applicability of his model and lead to reasonable δ values for n-amyl alcohol in sodium perchlorate[52] but require the solution of an integral equation by successive approximations, just as in his earlier treatment of specific ionic adsorption. These changes would seem at least as appropriate for the analysis of the NaF thiourea data,[51] however as for the n-amyl alcohol, since there is probably less specific ionic adsorption for NaF than for sodium perchlorate and the introduction of the average dielectric constant is less satisfactory when ionic adsorption is present. Further, since even Devanathan's improved treatment is not easily amenable to inclusion of some of the omitted effects mentioned above, a more satisfactory method will be outlined later.

Another method of obtaining $\Gamma(q)$ is to establish a two-dimensional equation of state for adsorbed species, then obtain $\Gamma(q)$ from the surface pressure.[58] This method, which will not be discussed herein, has been applied by Parsons[57] to Schapink *et al.*'s thiourea data and the dependence of the p.d. across the inner layer plotted vs. Γ for fixed q. The results are of the form

$$V_1 = (q/K_0) - (\Gamma/D), \tag{2.3.3}$$

where K_0 is the integral capacitance of the inner region for $\delta=0$ and D is found to decrease markedly as q becomes more negative. Parsons expressed D as $\varepsilon_1/4\pi\mu_p$, but it seems more correct to write $D=[4\pi<\mu_p(\mathscr{E}_p)>/\eta]^{-1}$, suggesting that the thiourea dipole is either not fully pinned or that η varies appreciably. Parsons instead considers that ε_1 varies with q and finds that it changes from 11·4 at $q=0$ μC/cm^2 to 7·60 at $q=-12$ μC/cm^2. He also finds a somewhat similar change in a kind of differential dielectric constant obtained from the change in standard free energy of adsorption with q, but here again it is assumed that $<\mu_p(\mathscr{E}_p)>=\pm\mu_p$.

In 1926, Frumkin[59] proposed the relation

$$q = (1-\delta)q_d + \delta q_p \tag{2.3.4}$$

in a treatment of the effect of neutral-substance adsorption on electrocapillary curves. Here q_d is the charge when $\delta=0$, while q_p is that when $\delta=1$ and the inner layer consists only of adsorbed neutral molecules (other than those of the solvent). Both q_d and q_p are to be evaluated at the same total double-layer p.d. Equation (2.3.4) assumes that for charge (or static capacitance) calculations, the charge of the adsorbed neutral molecules covering a fraction δ of unit area of the electrode is just the factor δ times the charge of a complete monolayer of neutral molecules at the given polarization p.d. Further, it is separately assumed that the charge per unit area associated with regions where there is no neutral molecule adsorption is independent of the amount of such adsorption.

It is clear that (2.3.4) will approach exactitude as $\delta \to 0$ or as $\delta \to 1$. We believe that it is likely to be very good in the intermediate δ region as well provided q_d and q_p are both taken dependent on δ because of planar interaction effects. This approach still involves continuous charge distributions and so will not be useful in calculating δ vs. q or V_0 *ab initio*, but it does avoid the previous necessity of smearing out the properties of an inner region composed of two or more different species and describing it in terms of averaged quantities which may depend on δ. Instead, as we shall show later, q_d vs. V_0 and q_p vs. V_0 may be calculated separately (except for planar interaction effects) using appropriate values of dipole moment, thickness, natural field, and compressibility for each separate calculation.

One probably minor defect in equation (2.3.4) is its neglect of any variation of the specific area of adsorbed molecules with increased compaction in the layer.[59] Any such dependence of specific area on δ requires that the total charge in (2.3.4) be computed on a molecular number rather than on an area basis.

Let $\tilde{C}_d$ and $\tilde{C}_p$ be the differential capacitances of the double layer when $\delta = 0$ and 1, respectively, and $(\mathrm{d}\delta/\mathrm{d}V_0) = 0$. Then differentiation of (2.3.4) with respect to V_0 yields

$$\tilde{C} = (1-\delta)\tilde{C}_d + \delta \cdot \tilde{C}_p + (q_p - q_d)(\mathrm{d}\delta/\mathrm{d}V_0), \tag{2.3.5}$$

which shows that although the static capacitances are in parallel, the variation of coverage with polarization introduces a coupling in the differential capacitance between the two contributions. On rewriting $\mathrm{d}\delta/\mathrm{d}V_0$ as $(\mathrm{d}\delta/\mathrm{d}q)$ $(\mathrm{d}q/\mathrm{d}V_0)$, (2.3.5) may be alternatively written

$$\tilde{C} = \frac{(1-\delta)\tilde{C}_d + \delta \cdot \tilde{C}_p}{1-(q_p - q_d)(\mathrm{d}\delta/\mathrm{d}q)}. \tag{2.3.6}$$

Equation (2.3.4) has been used by Breiter and Delahay[52] to analyze their n-amyl alcohol data and leads to satisfactory agreement with δ values obtained by the electrocapillary method. They have also obtained consistent results with (2.3.5) applied in regions where the $(\mathrm{d}\delta/\mathrm{d}V_0)$ term may be neglected. This term has been omitted by Parsons[60] in a consideration of adsorption isotherms, and he shows such omission leads to inconsistency with most isotherms. Hansen, Minturn, and Hickson[61, 62] have applied equations (2.3.4) and (2.3.5) together with a specific form of adsorption isotherm and dependence of q_p on V_0 given by Frumkin[59] to obtain an explicit expression for $\bar{C}$. This was then used to define an apparent δ, essentially by omitting the last term in (2.3.5), obtaining $\delta_{\text{app}} = (\bar{C}-\bar{C}_d)/(\bar{C}_p-\bar{C}_d)$. Analysis of adsorbed organic compounds led to $\delta_{\text{app}} \lessdot -2$ under some conditions, showing the importance of the omitted term in keeping $\delta \geqq 0$.

Finally, it may be mentioned that if the q_d and q_p terms in (2.3.4) are calculated separately, there is no guarantee that the p.d. V_2 across the diffuse layer will be the same in both regions. When it is different, it is of course not proper to separate out the effect of the diffuse layer and treat an inner region separately. This is not a limitation but a virtue of equation (2.3.4) and the separate calculation of q_d and q_p. Experimentally, all one can be sure of is that the same total p.d. V_0 is applied across the double layer. In regions where there is neutral substance adsorption, V_1 and V_2, but not their sum, will be different from the V_1 and V_2 where there is no such adsorption. The diffuse region must be treated separately for each region and the OHP will lie at a somewhat different distance from the electrode for each. Since individual hydrated ions in the diffuse region may be expected to have considerable freedom of motion in all directions except that toward the electrode, the different mean V_2's across the δ and $(1-\delta)$ fractional areas imply that on the average there is some difference in diffuse-layer charge in the two regions. Until the diffuse-layer charge in both regions is high, so the corresponding diffuse region capacitances make a negligible contribution to the total capacitance, it will not be accurate to consider a single (averaged) diffuse layer as Parsons has done.[57] Perhaps this is one reason why he finds a variation of ε_1 and inner layer thickness with charge. Another reason, in addition to that discussed after equation (2.3.3), may be that the use of the q/K_0 term with constant K_0 implies the independence of Γ of the p.d. arising from adsorbed water molecules. As already mentioned, this will not be a good approximation over most of the δ range.

3. DISCRETENESS OF CHARGE EFFECTS

In this Section we shall consider some treatments of specifically adsorbed ions of a single sign only. Of especial interest is the dependence of quantity adsorbed on ionic concentration in the bulk of the solution and on electrode charge or applied p.d. For simplicity, we shall consider the adsorption of monovalent anions of a single type only.

Stern[25] originally treated the general specific adsorption situation using the Boltzmann distribution law. His results have been considered by Grahame[20] and Parsons[22]. In the present case, they show that on the basis of Stern's analysis q_1 is given quite closely by

$$q_1 \cong -2rec_0[1-(q_1/q_{1m})]\exp(-w_1/kT), \tag{3.1}$$

where r is the radius of the non-solvated anion and c_0 is its bulk concentration. The quantity w_1 was defined by Stern to be the work necessary to move an ion from the interior of the solution to its adsorbed position at the IHP. Parsons[22] has identified w_1 as the standard electrochemical free energy accompanying adsorption and shows that (3.1) is based on a Langmuir adsorption isotherm.

The quantity w_1 may be formally separated into two parts by writing

$$w_1 = -e(\psi_1+\varphi_1), \tag{3.2}$$

where ψ_1 is the potential of the IHP relative to the solution and φ_1 is a specific adsorption potential for anions which may possibly depend on q but is expected to be essentially independent of q_1. There seems to be no completely unambiguous method of carrying out the separation in (3.2). If $\psi_1(q)$ can be calculated accurately from theory, taking the discrete nature of the adsorption process into account, then $\varphi_1(q)$ can be calculated using experimentally determined values of $q_1(q)$ and assuming (3.1) to be adequate. Unfortunately, there is a pitfall in almost every step of such a calculation.

The potential ψ_1 is a quantity of great importance. In the earlier work[20,25] discreteness of charge was neglected, and ψ_1 was taken as the mean potential of the IHP relative to the solution when the adsorbed ionic charge was smeared out in this plane. Then it becomes equal to the V_i of Fig. 5 and, on assuming the applicability of equations (2.2.4) and (2.2.6) with $\varepsilon_\beta = \varepsilon_\gamma \equiv \varepsilon$, is given by $(V_0 - V_\beta)$. This p.d., or $V_0 - V_\beta - V_2 = V_\gamma$, has become known as the macropotential.[63]

Frumkin[64] in 1933 first suggested that a proper theory of the double layer might require consideration of discreteness of charge effects. Esin and Markov[65] later observed that the shift of ecm potential with increase in concentration of ions which are specifically adsorbed was larger than could be explained on the basis of a smeared sheet of adsorbed ions. The problem is to calculate the actual adsorption potential ψ_1 when the discrete nature of the adsorbed charge layer is taken into account. This potential, the micropotential, has been variously rather loosely defined as the potential at the center of an adsorbed ion, the potential at a vacant ion position, etc. We believe it should more properly be defined as the potential relative to the solution at the position of the center of an adsorbed ion with that ion absent but all other charges, including image charges, as they would be in the presence of the ion. This definition is in substantial agreement with those of Grahame[50] and Ershler.[63]

The micropotential has been calculated in various approximate ways. Esin and Shikov,[66] Grahame,[50] and Levine, Bell, and Calvert[49] have considered a model where the adsorbed ions are hexagonally arrayed and are paired with their images in the electrode or in the diffuse layer. Their methods of analysis differ slightly but their results are in substantial agreement. The correction to V_i derived by Esin and Shikov turned out to overexplain the Esin–Markov effect. Therefore, Ershler,[63] and later Grahame,[50] Levich, Kiryanov, and Krylov[67] and Levine *et al.*,[49] used a model in which imaging of a hexagonal array of adsorbed ions takes place both in a perfectly conducting electrode and in the diffuse layer, taken as an equipotential at a distance $(\beta+\gamma)$ from the electrode and also with infinite dielectric constant. The greater the charge density in the nearest part of the diffuse region, the more nearly it can be approximated as an equipotential. All the above authors took $\varepsilon_\beta = \varepsilon_\gamma = \varepsilon$; it is not always clear whether the ε meant was actually ε_∞. Note that when imaging of the charges of specifically adsorbed ions occurs in both the electrode and the diffuse layer, an infinite set of images appears.

The inclusion of infinite imaging leads to better agreement than earlier treatments between theory and the shift of the ecm potential with concentration. When θ is less than approximately 0·3, about the limit of measurement in most solutions, the above treatments agree in predicting that the micropotential should be given quite closely by $V_i - [4\pi q_1 \beta\gamma/\varepsilon(\beta+\gamma)]$. Using this result, ψ_1 becomes

$$\psi_1 = \frac{4\pi\gamma}{\varepsilon}\,[q + q_1\{\gamma/(\beta+\gamma)\}] + \left(\frac{2kT}{e}\right)\sinh^{-1}\left(\frac{q+q_1}{2A}\right), \tag{3.3}$$

where (2.2.4) and (2.2.5) have been used with $\varepsilon_\beta = \varepsilon_\gamma = \varepsilon$. This result is, however, not very logically based since it combines mean p.d.'s with corrections based on departure from the smearing approximation. The discreteness of charge correction to V_i will be most accurate when $\theta \ll 1$ and each adsorbed ion is far away from other such ions. It is then reasonable to take as a first approximation $\varepsilon_\beta = \varepsilon_\gamma = \varepsilon = \varepsilon_1$, where ε_1 is the usual saturable dielectric constant including the effect of water dipoles. On the other hand, in the usual continuous charge approximation, it is not reasonable to take $\varepsilon_\beta = \varepsilon_\gamma$, for reasons discussed earlier, and these quantities should, in fact, depend on θ. Further, even with $\varepsilon_\beta = \varepsilon_\gamma$ the continuous charge approximation leads to $E_\beta \neq E_\gamma$ in general, while equation (3.3) is consistent, as we shall see, with a constant field and linear potential drop in the inner region.

Next, we note that from (2.2.3) and (2.2.6) with $\varepsilon_\beta = \varepsilon_\gamma = \varepsilon$, $V_0 - V_2 \equiv V_1$ may be expressed as

$$V_1 = \frac{4\pi(\beta+\gamma)}{\varepsilon}\,[q + q_1\{\gamma/(\beta+\gamma)\}]. \tag{3.4}$$

It then follows from (3.3) and (3.4) that

$$\psi_1 - V_2 = \{\gamma/(\beta+\gamma)\}\,V_1, \tag{3.5}$$

implying a linear potential dependence for the micropotential in the inner region. Note that we have taken especial care to denote average p.d.'s with the symbol V and have used the different symbol ψ_1 for a p.d. which involves the micropotential. The problem of correctly separating the two has apparently led to the difficulties concerning the inner-layer field of Mott and Watts-Tobin and Grahame and Parsons discussed in Section 2.2. Incidentally, the derivation by Mott, Parsons, and Watts-Tobin[34] of a potential term equivalent to that in (3.5) by writing $\mu \equiv e\gamma$ is not well founded for ionic adsorption; a detailed consideration of the micropotential, such as that above, is actually required.

All of the above difficulties arise from the lack of a double-layer theory in which the discrete nature of all charges, those specifically adsorbed and those in the metal and diffuse layer, is simultaneously taken into account and their thermal energy is included. Since we believe such a theory will be a long time in arriving, it appears best to use continuous-charge equations such as (2.2.3) to (2.2.6), to calculate mean potentials, fields, and smeared charges, and to use equation (3.3) with $\varepsilon = \varepsilon_1$ for the micropotential which relates amount of adsorption and electrode charge. It must be again emphasized that this is a patchwork procedure and not very satisfying. Further discussion of this matter is given in the last Section.

Grahame[50] has derived an equation analogous to (3.1) by considering both the specific adsorption of anions and the concomitant adsorption of cations in the diffuse layer. Under most conditions of interest his result reduces to

$$q_1 = -K\exp(e\varphi_1/kT)a_\pm \exp(e\psi_1/kT) = -K'a_\pm \exp(e\psi_1/kT), \tag{3.6}$$

where ψ_1 is given by (3.3) and K is a constant. This result is thus of very nearly the same form as (3.1) with (3.2) substituted therein and θ neglected compared to unity. Such neglect is equivalent to the use of a Henry rather than Langmuir adsorption isotherm. Detailed analysis by Grahame[28] and Grahame and Parsons[9] of KI and KCl data leads to a linear increase in φ_1 as q decreases from large positive values, a maximum in the neighborhood of $q=0$, and some decrease thereafter. Further, φ_1 is found to be larger for KI than for KCl. The decrease in chemical bonding of the chemisorbed halogen ions as q increases positively is contrary to expectation and almost certainly indicates the inadequacy of (3.6) or (3.3) or both. Another indication of weakness in these equations is that they lead to an appreciable decrease in $\gamma/(\beta+\gamma)$ as q decreases from large positive values.

In Watts-Tobin's[30] and Mott's and Watts-Tobin's[6] work, V_2 has been neglected and a Boltzmann distribution law for adsorbed anions (or anion–adatom complexes) has been employed. Watts-Tobin has taken the entire mean p.d. V_1 as the potential which enters into the electrostatic part of the adsorption energy. This assumption is modified in the work of Mott and Watts-Tobin where essentially the potential $\{\gamma/(\beta+\gamma)\}\, V_1$ is used, consistent with (3.4) and (3.5) when V_2 is neglected. Mott and Watts-Tobin have also derived, by considering imaging of adions in the electrode only and planar interaction, an added term in the micropotential intended to correct at least in part for failure, as θ increases, of the usual assumption that the micropotential can be derived from a linear potential variation in the inner region. In the present notation and using a corrected value for the correction term,[6] the result for q_1 is

$$q_1 = -aec_0 \exp\, [(e/kT)\{\varphi_1 + [\gamma/(\beta+\gamma)]V_1 - e\gamma^2(\pi\,|q_1|\,/\,e)^{3/2}/\varepsilon_\infty\}], \quad (3.7)$$

where a is here a length of the order of a molecular diameter. Although (3.7) does not agree, even after a change in notation, with the final expression given by Mott and Watts-Tobin, because of compensating errors in sign in their actual calculation, equation (3.7) was in fact employed and leads to their Fig. 12. The resulting theoretical q_1 vs. V_1 curve is in fair qualitative agreement with similar experimentally determined curves obtained by Grahame for a variety of specifically adsorbed anions. These curves are actually plotted against a p.d. which includes V_2 as well as V_1; comparison with a curve plotted vs. V_1 is not quite correct, but the change in shape arising from this difference should not usually be very important.

In Mott's and Watts-Tobin's treatment of the micropotential for adsorption of ions, the energy of adion–adion and adion–image interactions was calculated by smearing the adion image charges in their plane and similarly smearing the adions in their plane down to a distance equal to the mean distance between adions. This procedure is only approximate since it ignores discreteness of charge except insofar as the adion spacing is identified with a lower limit of integration. An improved discrete model calculation of the micropotential for the adsorption of ions follows from the work of Esin and Shikov,[66] Grahame,[50] and Levine *et al.*[49] in which adsorbed ions and their images are treated as dipoles or as parallel layers of discrete charge. In such single-image treatments, however, one is still neglecting infinite imaging in the diffuse layer and the electrode, discrete planar interaction between inner layer water molecules and adions, and the alteration of water–water dipolar interaction arising from the presence of nearby adions. Further, we wish to emphasize that the procedure of regarding adions and their images as dipoles, ideal or non-ideal,[42] is only valid in obtaining the contributions to the energy from adion–adion and adion–image interactions. It would be nonsense, for example, to base a calculation of the energy of interaction between the charged electrode and the adions upon a picture which replaces the adions with dipoles. Finally, Levine *et al.*[49] have pointed out that the inclusion of multiple imaging of adions in the electrode and in the OHP causes the planar interaction term, proportional to $(|q_1|/e)^{3/2}$ in any of the above treatments, to be essentially eliminated. This result also follows from Grahame's[50] earlier treatment and explains why no $|q_1|^{3/2}$ term appears in the micropotential expression (3.3). The appropriateness of including infinite imaging will be discussed in the last section.

Quite recently, Levine *et al.*[49] have considered discreteness of charge effects in detail and have derived a new relation between q_1 and q, etc. This was done by equating the chemical potential of a specifically adsorbed ion with that of a similar ion in the interior of the solution. Two refinements were incorporated. First, it was assumed that there were N_s adsorption sites per unit area on the electrode surface and that an adsorbed ion occupies p such sites, where p need not be integral. Further, it was recognized that adsorbed ions occupy sites which are unavailable to other adsorbed ions, a fact which alters their entropy of distribution and chemical potential. This effect was also independently recognized by one of the present authors (C. A. B., Jr.) and treated differently — see later discussion. Levine *et al.* have incorporated it into their theory by using the zero-order approximation to the entropy of mixing molecules of different sizes provided by the volume-fraction statistics of Flory and Huggins. There seem to be two difficulties in this procedure. First, the Flory–Huggins statistics are derived for three-dimensional mixing while the effect to which they are applied here is two-dimensional. Secondly, it is desirable to take into account simultaneously the competition for adsorption sites of inner layer water molecules and adsorbed ions.

In the present notation, the result of Levine *et al.* for adsorption of a univalent anion may be written as*

$$q_1 = -\left[\frac{a_- N_s e}{n_0}\right]\left[1+\frac{pq_1}{N_s e}\right]^p \exp\left[\left(\frac{e}{KT}\right)\{\varphi_1+\psi_1\}\right], \tag{3.8}$$

where ψ_1 is given by (3.3) with ε apparently equal to ε_1^0, a_- is the activity of the anion in the bulk of the solution, and n_0 is the concentration of water molecules. As pointed out by Levine *et al.* this result essentially reduces to that of Grahame, equation (3.6), when $p=0$. Further, it is clear that it essentially reduces to the Stern result, equation (3.1), when $p=1$. By using the specific values $p=1{\cdot}83$, $N_s=5\times10^{14}$ cm^{-2}, and $\gamma/(\beta+\gamma)=0{\cdot}4$, Levine *et al.* showed that Grahame's[28] KI data led to little or no variation of φ_1 with a_- or q and was consistent with a constant value of $\gamma/(\beta+\gamma)$. On the other hand, they found that Grahame's derived curve of V_2 vs. V_0 for 0·05 N KI could be fitted quite well by a value of $p=2$, $(\beta+\gamma)=5$Å, and $\gamma/(\beta+\gamma)$ again 0·4. The derived ε value for the inner layer, which was taken independent of q, varied appreciably with solute concentration, however.

The above results certainly suggest that (3.8) is considerably superior to earlier formulas in which $p=0$ and possibly even to those for which $p=1$. On the other hand, the use of volume statistics for a surface problem, the omission of consideration of the role of water molecules, the neglect of any variation of ε with density or saturating field, the omission of any dependence of β and γ on inner-layer pressure, the omission of some planar-interaction effects, and the use of equation (3.3) for ψ_1, which is based on a combination of mean p.d.'s and discrete-charge p.d.'s, suggest that there is even yet considerable room for improvement in the treatment of the present problem.

Finally, it is worth mentioning that in recent work Parry and Parsons[68] have used the Stern result ($p=1$), equation (3.1), to analyze the specific adsorption of benzene *m*-disulphonate ions. It is found that φ_1, the specific adsorption potential, is independent of both q and q_1 provided the $\gamma/(\beta+\gamma)$ term appearing in (3.3) is allowed to vary with q_1. A distinction

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*We have written the result in a slightly different form from that of Levine *et al.* to avoid the appearance of terms like $(-N_s e)^{p-1}$, which may lead to complex numbers for p non-integral.

is made between $\gamma/(\beta+\gamma)$, which measures the proportion of V_1 involved in the micropotential (equation 3.5), and the actual distance ratio $(x_2-x_1)/x_2$, where x_2 is the distance between the electrode and OHP and x_1 is the separation between the electrode and the IHP. This latter ratio is found to be 0·25 and nearly independent of q_1. This distinction is made in an attempt to correct for the expected failure of the constant-field approximation in the inner layer (see earlier discussion). If it could be certain that φ_1 should actually be entirely independent of q and q_1, the variation in $\gamma/(\beta+\gamma)$ obtained by Parry and Parsons (about 0·3 to 0·9) would be meaningful within the limitations mentioned in the preceding paragraph. Actually, it seems possible that φ_1 might increase somewhat with increase in q because of increased covalent bonding and might decrease with increase in $|q_1|$ unless the increased planar interaction as θ increases is explicitly included in the theory.

4. FURTHER IMPROVEMENTS

In Section 2, some improvements were discussed of earlier equilibrium double-layer theories for the case of no specific adsorption. When there is no specific adsorption of ions, adatoms, or even of other dipolar molecules, the inner region of the double layer is composed of material all of the same species, such as water in the case of aqueous electrolytes. Even in this simplest situation, we have seen that when compression and planar interaction effects are even approximately included the result is relatively complicated.

In the present Section, we shall outline an improved approximate means of analyzing the situation where the inner region contains two different species having different permanent dipole moments and polarizabilities. Insofar as the effects of specifically adsorbed ions imaged in the electrode or of adatoms may be approximated by their effective permanent and induced dipole moments, this approach will apply to these cases as well as that of the adsorption of neutral substances at the interface. Note, however, that in the following treatment it will be assumed that the centers of dipoles of different species lie in the same plane. This will not be the case when the species are water molecules in the inner layer and adion-image dipoles. Such displacement will have some effect on nearest-neighbor planar interactions but will be less important for farther interactions.

If planar interaction could be neglected between the moments of a molecule of species X adsorbed in a surface region where it is almost entirely surrounded in the plane by molecules of species Y with the induced and permanent moments of the latter, to good approximation the problem could be handled using Frumkin's q-formula, equation (2.3.4). It would also be applicable whether species X were uncharged or charged. In this case, the calculation of q_d and q_p for the same applied V_0 could proceed independently by the methods of Section 2, and q finally calculated for a given δ (or θ in the case of adsorbed ions) using (2.3.4). This procedure would yield a q–V_0 curve for each neutral substance concentration, which could be compared with the experimentally determined results. The δ values used would need to be found independently by a separate method, such as that used by Parsons.[57,58] Alternatively, the experimental q–V_0 curves could be used to obtain δ vs. q or V_0 for each concentration, again using equation (2. 3. 4).

Unfortunately, it appears likely that in general the planar surroundings of an adsorbed molecule or ion will have an important effect on its own electrical behavior in the double layer. If this is the case, it is clearly a poor approximation to cluster all adsorbed molecules of a given species together and calculate their q_i–V_0 behavior without regard to the presence of molecules of different species. We believe, however, that it will still be a better approximation than any previously considered to take account first of the planar interactions and consequent coupling between the effects of molecules of the two different species, then to set up expressions relating V_0 and q_d and q_p separately, and finally to apply the Frumkin relation (2.3.4).

Because of planar interaction, the V_0–q_d and V_0–q_p relations will no longer be independent, but each will involve the parameters of the other. In this more complicated case, it is not possible to assume δ and calculate the q corresponding to a given V_0. Instead, in order to satisfy the two mutually dependent V_0 relations simultaneously, we use experimental V_0–q values and determine that δ value which leads to such satisfaction. In general, this will be a complicated procedure which will only be practicable with a digital computer. For given electrolyte and neutral-substance bulk concentrations, one will finally obtain theoretical values of δ to compare with those determined independently. If there is appreciable difference, constants of the model can be adjusted until good agreement over the whole range is achieved. A sufficient but not absolutely necessary condition for this to be possible for many ranges of concentrations and temperature is that the model analyzed bear a close resemblance to the actual situation and that the approximations introduced be sufficiently well justified.

It should be emphasized that one does not have unlimited flexibility in adjustment of constants. When the concentration of neutral substance is zero, one has only one species in the inner region (if simultaneous ionic adsorption and/or adatom formation is prohibited or absent) and the constants needed in the V_0-q_d relation may be selected by curve fitting under this condition. These constants should then remain fixed while those necessary in the V_0-q_p relation are determined from curve fitting when the neutral-substance concentration is non-zero. The final complete set of constants should then lead to good curve fitting for wide ranges of electrolyte and neutral-substance concentrations.

Although detailed curve fitting according to the above procedure will be presented elsewhere, we shall here briefly outline some of the approximations and considerations which seem reasonable. First, if the sizes of the two different species of molecules are not greatly different, it will be a good approximation to take N as before as the maximum number/unit area of molecules in the inner region and to consider that N remains constant as δ varies. This will be an excellent approximation for $\delta \approx 0$ or $\delta \approx 1$ independent of the size ratio and will clearly be a better and better approximation in the intermediate δ region as the ratio approaches unity. It will also be a good approximation for all δ if the molecules are not close-packed in the plane when the maximum surface coverage is attained but are somewhat separated from one another because of the presence of isolated adsorption sites and/or of dipolar and other repulsive forces. In this case, they may probably still be considered to be in a hexagonal or square array, but their minimum distance apart will not be primarily determined by steric effects; thus, their actual size ratio will not be of primary importance. The relaxing of our foregoing close-packed assumption makes the present situation less applicable to electrolyte double-layer calculations, but it should be pertinent to adsorption from diffuse gas phases since the dielectric properties of the gas itself may then be neglected.

When N is taken independent of δ, the term $[<\mu> + (\mathcal{P}_1/N_v)]/r_0^3$ which appeared in the zero-specific-adsorption treatment of Section 2 will still involve $N^{3/2}$ but $[<\mu> + (\mathcal{P}_1/N_v)]$ must be changed whenever $\delta > 0$. If N_i and A_i are the number/unit area and specific effective molecular area of the ith species, then $\delta \equiv N_p A_p/(N_p A_p + N_d A_d)$. For the interaction of a given molecule with its surrounding molecules, it is the number of these molecules of different types, not their surface area, which is important. Let us therefore define $\delta' \equiv N_p/(N_p + N_d) = \delta/[\delta + (A_p/A_d)(1-\delta)]$. In the $\delta \neq 0$ case, we believe it will be a good approximation to consider average surroundings and to replace $[<\mu> + (\mathcal{P}_1/N_v)]$ by $(1-\delta')$ $[<\mu_d(\mathcal{E}_d)> + (\mathcal{P}_{1d}/N_{vd})] + \delta'[<\mu_p(\mathcal{E}_p)> + (\mathcal{P}_{1p}/N_{vp})]$. It is this replacement in the calculation of $\mathcal{D}_d$ and $\mathcal{D}_p$ which leads to the coupling between the electrical effects of the two kinds of molecules. In addition to the appearance of direct coupling in the V_0-q_d and V_0-q_p equations, it also turns out to appear in the expressions for the orienting fields $\mathcal{E}_d$ and $\mathcal{E}_p$ themselves. Note that either μ_d or μ_p may be identically zero in the present general treatment.

Although we shall not give the rather complicated equations here, it is worth mentioning that when $\delta' \ll 1$, they can be approximately reduced to an expression somewhat like (2.3.2). In particular, direct dependence of the second term on $\Gamma \equiv \Gamma_p$ is then found, but the term $<\mu_p(\mathcal{E}_p)>/\eta$ with η a constant is replaced by a much more complicated expression which involves induced polarizabilities, $<\mu_p(\mathcal{E}_p)>$, $<\mu_d(\mathcal{E}_d)>$, q_d, and q_p. Future numerical work may show that further simplification may be possible for a limited range of δ' or δ, but it appears that the use of (2.3.2) to obtain $<\mu_p(\mathcal{E}_p)>$ or even $<\mu_p(\mathcal{E}_p)>/\eta$, where η is a constant, is usually a hazardous and unwarranted operation.

We have referred throughout this paper to the practice of many workers of considering the charges in the inner layer as being imaged both by the metal and by the diffuse layer of ions; some further comment is needed on this point. To begin with, let us assume that the diffuse layer is indeed a good imaging plane. Then, there will result an infinite set of images for every elementary charge in the inner layer; thus, all inner-layer dipoles will be imaged as well as ions, and it is the resulting set of image monopoles and dipoles upon which the micropotential will depend. Since adions will very likely retain part of their solvation shells containing highly polarized dipoles, we feel that a proper calculation, taking simultaneous imaging of both adions and dipoles into account, might produce results appreciably different from treatments in which such dipole imaging is neglected. Note that neglecting imaging of the solvent dipoles is just another aspect of the basic approximation of neglecting all or part of the discrete structure of the system.

Secondly, even if one neglects solvent dipole imaging and makes the risky approximation of replacing the inner-layer solvent by a homogeneous medium of dielectric constant different from unity, the quoted results of several workers require some further discussion.[69]

Grahame[50] has calculated the micropotential for the infinite imaging case making the assumption that the local field is uniform throughout the inner layer; that is, that the potential varies linearly with distance from the electrode. This assumption is sometimes quite far from correct, particularly for high coverages and/or $\beta/\gamma \gtrsim 1$, and leads to the absence of terms in the micropotential proportional to $|q_1|^{3/2}$ and higher order in $|q_1|$ which must become important in the above limits. He furthermore makes two errors in his treatment of the total p.d. across the inner layer which by coincidence are exactly compensating, making his expression for the total inner layer p.d. fortuitously exact. Furthermore, Levich, Kir'yanov, and Krylov[67] in an apparently exact treatment have found that for coverages less than 25–30 per cent and (necessarily, although this was not explicitly stated in the brief communication of Levich *et al.*) for $\beta \approx \gamma$ the uniform field approximation is very good. Outside of this range the situation is not so clear. Unfortunately, length restrictions prevent us from enlarging upon the above comments in the present work; however, we shall present a detailed analysis and numerical results for some cases where β and γ are not nearly equal in a future communication.[69]

A question more fundamental in a sense than those we have just been considering is the pertinence of considering imaging in the diffuse layer of ions at all. We feel that even this is in some doubt; in any case the procedure must certainly be regarded with suspicion when the Debye length of the diffuse layer is larger than either the mean adion separation or γ. In such a case, it appears that thermal motion within the diffuse layer would largely "wash out" the ionic imaging process leaving only bulk-watera imaging. Both the underlying faults in current infinite-imaging treatments and the absence of a theory which properly considers adions and solvent from a discrete viewpoint in the single-image regime lead us to the view that the Esin–Markov effect is as yet inconclusive evidence for the importance of infinite imaging.

Finally, we should like to point out a deficiency in conventional adsorption theory based upon the Boltzmann factor. The general practice in obtaining adsorption isotherms from statistical theory is to assume that the distribution function describing the system contains the usual Boltzmann factor and that the chief theoretical problem is the calculation of self-consistent micropotentials to go into this factor. When one considers, however, that in many instances the adsorbed phase is a two or more component mixture in which, because of the competition between the different species for occupation of the "completely filled" surface, the conditions leading to Boltzmann statistics are no longer present, it becomes apparent that a first-principles statistical treatment is desirable. The goal of such a treatment would be the determination of the proper expression to take the place of the Boltzmann factor and the establishment of the region in which that proper factor would be well approximated, as in a significant range it must be, by the Boltzmann factor. Thus, such a re-examination of the statistical mechanics of adsorption in multicomponent systems in which the different species may differ as to size, charge, and other properties, would be quite independent of the rather involved question of the correct choice for a micropotential. This independence of the problem presently considered from that of choosing the appropriate micropotential means, of course, that one may consider, up to a point, charged and uncharged objects on exactly the same footing.

The present authors have carried out such a program and find that the task was quite straightforward. The procedure essentially involved the counting of complexions leading to a given system condition with a constraining relation requiring that the total coverage of the active surface be complete. The microcanonical ensemble was used; however, it has been shown that the canonical ensemble leads to the same conclusions.[70] The chief results, insofar as we have examined them up to this time, indicate that the adsorption of a given component properly approaches Boltzmann behavior in the limit of zero adsorption of that component; however, as the adsorption increases, the competition and saturation effects cause appreciable departure from the usual expressions based on Boltzmann statistics.

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APPENDIX

TABLE 1. COMPARISON OF SYMBOLS USED BY VARIOUS AUTHORS

Author, (Reference number)	Symbols												
Present work	q	q_1	q_2	d	β	γ	V_0	V_β	V_γ	V_1	V_2	V_i	ψ_1
Macdonald, (2) Macdonald and Barlow, (4)	q			d			V_0			V_1	V_2		
Levine, Bell and Calvert, (49)	σ_0	σ_β	σ_d	d	β_*	γ	ψ_0				ψ_d	ψ_β	ψ_Δ
Watts-Tobin, (30)	σ			d	d'	l	φ			φ	neglected	$[\varphi]$	φ
Mott and Watts-Tobin, (6) Mott, Parsons, and Watts-Tobin, (34)	σ, q	$-en_i$	en_0	$(\beta+\gamma)$	β	γ	$-\psi$			$-\psi$	neglected		$-\lambda\psi = -\gamma\psi/(\beta+\gamma)$
Grahame, (20)	$q, -\eta$	η^i	η_d				ψ^r				ψ^0	$[\psi^i]$	ψ^i
Grahame, (50) Grahame, (28) Grahame and Parsons, (9)	q	$-\sigma$ $-n^i$ $-n_i$, $-n^i$		$(\beta+\gamma)$	β	γ	$(\psi^u + \psi^0)$	ψ'	$[\psi^\Delta]$	ψu	ψ^0	$[\psi^i]$	$\psi^i = (\psi^\Delta + \psi^0)$

Author, (Reference number)	Symbols												
Parsons, (22)	q^M	q^S_{1-2}	q^S_{2-S}	x_2	x_1	(x_2-x_1)	$(\varphi^M-\varphi^S)$				$(\varphi_2-\varphi^S)$	$[\varphi_1-\varphi^S]$	$(\varphi_1-\varphi^S)$
Parsons, (58)										$(\varphi^M-\varphi_2)$			
Parsons, (60)	q	q'					φ^{M-s}			φ^{M-2}			
Parsons, (57)				x_2									
Parsons, (24)	q	q^1		x_2	x_1	(x_2-x_1)	φ^M			$(\varphi^M-\varphi_2)$	φ_2		φ_1
Devanathan, (29)	$-q$	q_1	q_{2-S}	x_2	x_1	(x_2-x_1)	φ_m				φ_2	φ_1	
Devanathan, (54)	$-q$, q_{Hg}										φ_{2-S}		

In Table 1, the zero of V_0 is generally taken at the point $q=0$ in the absence of specific adsorption. When the same quantity appears in more than one column of a given row, the author in question did not distinguish between the different quantities involved. Square brackets are used where the author did not distinguish or did not distinguish properly between mean potentials and micropotentials (see discussion in text).

TABLE 2. COMPARISON OF ESTIMATED DOUBLE-LAYER PARAMETERS AT 25°C.

Author, (Reference number)	Material	ε_1^0	ε_∞	$\frac{d_0}{(\beta+\gamma)}$	β	γ	$\frac{\gamma}{(\beta+\gamma)}$
Macdonald (2)	NaF	15	5	4·6			
Devanathan (29)	Various	7·19	7·19	3·72	Crystallographic radius of adsorbed ion		
Grahame (28)	KI						0·3–0·8
Grahame and Parsons (9)	KCl						0·1–0·5
Parsons (57)	NaF Thiourea	14·9, 11·4		3·60–4·70			
Watts-Tobin (30)	(NaF)		1,2	3·45	(0·69)	(2·76)	(0·8)
Mott and Watts-Tobin (6)			3	4	2	2	(0·5)
Macdonald and Barlow (4)	NaF	14·9	6	4·4			
Levine, Bell and Calvert (49)	KI	10–20		5	(3)	(2)	0·4

In Table 2, a number of the values are only rough estimates; also, values not explicitly given by the authors but derivable from their work are given in parentheses. Distances are given in Ångstrom units.

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49. Levine, S., Bell, G. M. and Calvert, D., *Canad. J. Chem.* **40**, 518 (1962). The ε appearing on p. 52 is the dielectric constant of the solution in the diffuse layer. The sign in the exponent in (2.13) should be negative. The quantity $16\mu C/cm^2$ below equation (3.14) should be replaced by $20\ \mu C/cm^2$. The numerical values of $K_1(\pi\tau)$ presented in Table I are 10 times too small. The word "macropotential" below equation (3.16) should be "micropotential". The minimum in ψ_d (or maximum in $|\psi_d|$) vs. ψ_0 discussed on pp. 532 and 534 is actually (see Fig. 8) a maximum in ψ_d; it is also predicted by earlier theories with $p=0$. The factor multiplying K_1 in equation (A.8) should be $2\tau/\pi(2y-1)$. Reference 5 is incorrect and should be replaced by Ref. 67 of the present work.
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