

Theory of the Differential Capacitance of the Double Layer in Unadsorbed Electrolytes

JAMES ROSS MACDONALD

Texas Instruments Incorporated, 6000 Lemmon Avenue, Dallas 9, Texas

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A partly phenomenological, one-dimensional theory is presented of the double layer formed at an ideal polarized electrode in uni-univalent aqueous electrolytes showing no specific adsorption. The system analyzed consists of the metallic electrode with its surface charge density, a charge-free layer next to the electrode, and a diffuse layer containing positive and negative charges in unequal concentration extending into the body of the electrolyte. The theory includes the effect of dielectric saturation in both layers due to the field produced by an applied negative bias potential, and compression of the charge-free layer by this field is also taken into account.

The theory is compared with experimental data of D. C. Grahame on 0.916 N to 0.001 N NaF, which shows little or no adsorption on negative polarization. Good agreement is found both for the dependence of the differential capacitance of the entire system on negative polarizing potential (measured from the electrocapillary maximum) and on concentration. Such agreement allows several constants of the charge-free layer to be obtained relatively accurately. In particular, values for its initial thickness, modulus of linear compressibility, initial dielectric constant, and dielectric saturation constant are obtained. Comparison of these results with corresponding results for bulk water affords strong evidence that the charge-free layer consists of a single molecule of water and thus that cations nearest the polarized electrode are hydrated.

INTRODUCTION

THE study of the electrical double layer in electrolytes has been recognized for a long time as a fruitful avenue of investigation of the microscopic properties of solute and solvent. The experimental and theoretical work of Grahame¹⁻³ over the past ten years has done much to clarify the physical situation in an electrolyte adjacent to an ideal, polarized metallic electrode. Since such an electrode is blocking and will not allow conduction current to flow in either direction at the junction with the electrolyte, a final static distribution of charge in the electrolyte will eventually be reached after a potential difference is established between the electrode and the bulk of the electrolyte. It is, of course, necessary in practice that the applied potential difference be sufficiently small that there is negligible hydrogen evolution at the electrode in order that the electrode approximate ideal polarized behavior; we shall assume that this condition is always satisfied.

The double layer which is established near the metallic electrode is generally considered³ to consist of four regions, and so is really not a double layer at all. These regions comprise the metallic electrode, on whose surface there may be an excess or deficit of electrons, an inner region next to the electrode into which the electrical centers of ions cannot move because of their physical size, a further region accessible to the electrical centers of anions but not of cations, and a final region of the diffuse type containing both anions and cations in differing concentrations. If there is a layer of anions in the third region at their distance of closest approach to the electrode, this layer is termed the adsorbed

layer because the anions are held not by simple Coulomb forces but by specific short-range forces.

The presence of specific adsorption considerably complicates an analytical treatment of the double layer problem. In the present work, we shall therefore consider only those situations where such adsorption is absent. The double layer then consists of surface charge on the electrode, a charge-free region next to the electrode, and a diffuse region extending on into the bulk of the electrolyte. This situation is found experimentally on negative polarization of such solutes as NaF whose anions are not specifically adsorbed at a mercury electrode.¹

The diffuse layer has been fully treated theoretically by Müller,⁴ Grahame,^{1,2} and the present author together with M. K. Brachman.⁵ A theoretical analysis of the entire system without adsorption has not as yet been given. Grahame has, however, treated the problem by combining theoretical results for the diffuse layer with experimental results for the initial charge-free layer.¹ A theoretical treatment of the charge-free layer as well as the diffuse layer should allow some of the properties of the initial layer to be deduced by comparison of theory and experiment. The present work is designed to allow such information to be obtained and treats the entire system in a theoretical, although partly phenomenological, fashion.

The simplest measurements that can be carried out on the entire electrode-electrolyte system are determinations of the dependence of the differential capacitance of the whole system C_T^d on static bias potential and on electrolyte concentration. It is found that the resulting curves are quite complex even in the absence of adsorption. Present qualitative explanations of their

¹ D. C. Grahame, *Chem. Revs.* **41**, 441 (1947).

² D. C. Grahame, *J. Chem. Phys.* **18**, 903 (1950).

³ D. C. Grahame, *Comptes Rendus de la III^e Réunion, Comité International de Thermodynamique et de Cinétique Electrochimiques*, Berne, 8-12 August, 1951. References to further work of Grahame and others will be found in these first three references.

⁴ H. Müller, *Cold Spring Harbor Symposia Quant. Biol.* **1**, 1 (1933).

⁵ J. R. Macdonald and M. K. Brachman, *J. Chem. Phys.* **22**, 1314 (1954).

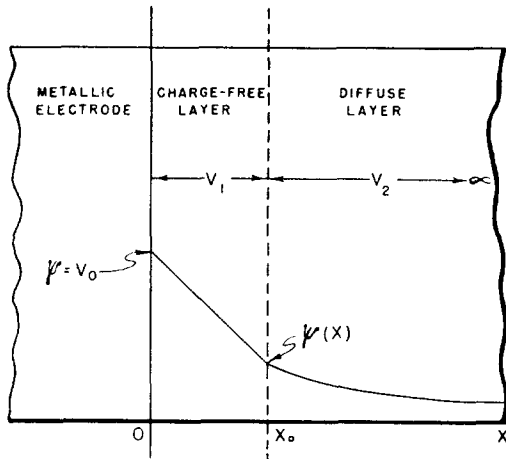


FIG. 1. Schematic representation of the electrical double layer without specific absorption. The dependence of the potential ψ on position is shown for positive polarization ($V_0 > 0$).

complicated dependence by Grahame³ and others include the effects of high-field dielectric saturation and of high-field compression of the charge-free layer, increasing as the polarizing potential is increased. Both of these phenomena are included in the present theory, and it is found that they can indeed explain many of the experimental results.

The matter of potentials between different phases in the system is fairly complicated and is dealt with at length by Grahame.¹ For our purposes, it is only necessary to know that when the applied potential between the polarized electrode and the body of the electrolyte is equal to the electrocapillary maximum potential, there is no surface charge on the polarized electrode.¹ We shall therefore choose to measure applied potential V_0 from this point and specify that the surface charge is zero at $V_0 = 0$.

The one-dimensional system which we shall analyze is shown in Fig. 1. An ideal polarized metallic electrode is placed at $x = 0$. This electrode is blocking for both positive and negative charge carriers. Next to this electrode there is a charge-free layer extending to $x = x_0$. Finally, polar material containing univalent positive and negative charge carriers extends from $x = x_0$ to $x = \infty$. The dielectric constants in the two layers may be different and may depend on electric field strength and position. Also, the thickness x_0 of the charge-free layer may be a function of electric field strength. We are interested in the dependence of the differential capacitance C_T^d of this whole system on the applied dc bias potential V_0 and on the bulk concentration of the charge carriers. As shown in the figure, the zero of potential is taken at $x = \infty$, and the potential drop across the charge-free layer designated as V_1 , that across the diffuse layer by V_2 . The mean local potential inside the material ψ will thus be zero at $x = \infty$ and equal to V_0 at $x = 0$.

In order to simplify the succeeding work, we shall

introduce the following normalized quantities: $\psi^* = \psi / (kT/e)$; $V^* = V / (kT/e)$; $\mathcal{E}^* = \mathcal{E} / (kT/eL_D^0)$; $\rho^* = \rho / 2c_0e$; $\sigma^* = \sigma / (kT/e)$; $z = x/L_D^0$. In these expressions \mathcal{E} is the mean local field strength within the material, ρ the volume charge density, and σ a surface charge density. The normal concentration of positive or negative ions in the bulk of the material far from the electrode is c_0 , and the Debye length L_D^0 in the diffuse layer is given by $[\epsilon_2^0 kT / 8\pi c_0 e^2]^{1/2}$ for zero applied voltage. In this expression, ϵ_2^0 is the static dielectric constant in the diffuse layer for $V_0 = 0$. In general, we shall use a superscript zero to designate the value of a quantity at zero potential and the subscripts one and two to identify quantities defined in the charge-free and diffuse layers, respectively.

CONDITIONS IN THE DIFFUSE LAYER

In order to obtain the differential capacitance of the complete system, it is necessary to determine the charge and potential distributions within the system when an external bias potential is applied. It will be most convenient to consider first conditions within the diffuse layer. The dependence of charge density on potential in this layer may be obtained either from the Debye-Hückel equations⁵ or by potential energy considerations.^{1,4} The result obtained is

$$\rho^*(z) = -\sinh \psi^*(z). \quad (1)$$

This result holds for either anodic or cathodic polarization. If a positive potential is applied to the electrode at $x = 0$, V_2^* , ψ^* , and \mathcal{E}^* will all be positive quantities.

Next, we need to know the dependence of \mathcal{E}_2^* , the normalized field strength in the diffuse layer at $z = z_0$ on V_2^* . To obtain this result we shall require expressions for the dependence on field strength of the static dielectric constant and the differential dielectric coefficient. These quantities are defined by $\epsilon = D^* / \mathcal{E}^*$ and $\kappa = dD^* / d\mathcal{E}^*$, respectively, where D^* is the normalized electric displacement. They therefore satisfy the relation

$$\mathcal{E}^* \frac{d\epsilon}{d\mathcal{E}^*} = (\kappa - \epsilon). \quad (2)$$

Grahame² has given a rather complete discussion of dielectric saturation effects in the diffuse layer, and we shall draw heavily on his work for the results of the present section. In particular, since there is no adequate fundamental theory of dielectric saturation in a polar material, we shall use Grahame's heuristic formula for field-strength dependence

$$\kappa = c_2 + a_2 [1 + 2b_2 \mathcal{E}^{*2}]^{-1} = c^2 + a_2 [1 + 2b_2^* \mathcal{E}^{*2}]^{-1}, \quad (3)$$

where c_2 , a_2 , and b_2 are constants. Grahame actually considers a family of equations similar to (3) and decides that the form (3) is one of a number of reasonable choices which will fit experimental data on electrolytes. We choose the specific form (3) because it lends

itself to algebraic and numerical calculations. Note that if b_2 is independent of concentration, $b_2^* \equiv (kT/eLD^0)^2 b_2$ will depend thereon because of the presence of LD^0 .

The effective static dielectric constant may be derived from (3) by integration. We find, using Eq. (2),

$$\begin{aligned} \epsilon &= \frac{1}{\mathcal{E}^*} \int_0^{D^*} dD^* = \frac{1}{\mathcal{E}^*} \int_0^{\mathcal{E}^*} \kappa d\mathcal{E}^* \\ &= c_2 + a_2 [(2b_2^*)^{1/2} \mathcal{E}^*]^{-1} \sinh^{-1} [(2b_2^*)^{1/2} \mathcal{E}^*]. \end{aligned} \quad (4)$$

It follows that when $\mathcal{E}^* = 0$, $\epsilon = \epsilon^0 = \kappa = \kappa^0 = a_2 + c_2$. Also, when $\mathcal{E}^* = \infty$, $\epsilon = \epsilon^\infty = \kappa = \kappa^\infty = c_2$. Thus, c_2 is the nonpolar contribution to the dielectric constant remaining after the polar contribution has been completely saturated. It is perhaps worth mentioning that the mean local field \mathcal{E}^* appearing in these expressions is that computed from the charge distribution at equilibrium after a dc potential has been applied so long that the initial charging current has died out.

The dependence of \mathcal{E}_2^* on V_2^* may now be obtained from Poisson's equation written in terms of normalized variables as

$$\begin{aligned} -\frac{dD^*}{dz} &= -\left\{ \mathcal{E}^* \frac{d\epsilon}{d\mathcal{E}^*} + \epsilon \right\} \frac{d\mathcal{E}^*}{dz} = -\kappa \frac{d\mathcal{E}^*}{dz} \\ &= \kappa \frac{d^2\psi^*}{dz^2} = -\frac{\kappa}{2} \frac{d}{d\psi^*} (\mathcal{E}^*)^2 = -\epsilon_2^0 \rho^*(z). \end{aligned} \quad (5)$$

Equation (2) was used in simplifying this equation. We now introduce Eq. (1) in (5) and integrate

$$\int_0^{\mathcal{E}_2^*} \kappa d(\mathcal{E}^*)^2 = -2\epsilon_2^0 \int_0^{V_2^*} \rho^* d\psi^* = 2\epsilon_2^0 \int_0^{V_2^*} \sinh\psi^* d\psi^*.$$

Using Eq. (3) for κ , we find

$$\begin{aligned} c_2 \mathcal{E}_2^{*2} - a_2/b_2^* + (a_2/b_2^*) (1 + 2b_2^* \mathcal{E}_2^{*2})^{1/2} \\ = 4\epsilon_2^0 \sinh^2(V_2^*/2). \end{aligned} \quad (6)$$

Equations formally identical to (4) and (6) have been given by Grahame.² Now let

$$\begin{aligned} u &\equiv (2b_2^*)^{1/2} \mathcal{E}_2^*, \\ B &\equiv (1 + u^2)^{1/2}, \end{aligned} \quad (7)$$

and

$$\eta = 2b_2^* \sinh^2(V_2^*/2).$$

We find from (6) that

$$B = -a_2/c_2 + [(\epsilon_2^0/c_2)^2 + (4\epsilon_2^0/c_2)\eta]^{1/2}, \quad (8)$$

and since from (7)

$$u = (B^2 - 1)^{1/2}, \quad (9)$$

we have succeeded in expressing \mathcal{E}_2^* in terms of V_2^* . If \mathcal{E}_2^* is known, we can compute u ; and from a curve of u versus η , then compute η . Finally V_2^* can be obtained most simply from the relation

$$\cosh V_2^* = 1 + \eta/b_2^*. \quad (10)$$

Of course, if V_2^* is known, the equations can be used directly to calculate \mathcal{E}_2^* . It is worth pointing out that, although \mathcal{E}^* will vary with position in the diffuse layer, thereby causing κ and ϵ to vary also, the calculation of the differential capacity of either the diffuse layer² or of the whole system requires only a knowledge of the functional dependence of \mathcal{E}_2^* on V_2^* .

CONDITIONS IN THE CHARGE-FREE LAYER

Since by definition there is no charge in the charge-free layer, we may solve Laplace's equation directly for this region with the boundary conditions $\psi^* = V_0^*$ at $z=0$ and $\psi^* = V_2^*$ at $z=z_0$. We assume that there is no discontinuity in potential at the plane $z=z_0$. Since $V_1^* = V_0^* - V_2^*$ is the potential difference across the layer, we obtain from Laplace's equation

$$\mathcal{E}_1^* = V_1^*/z_0, \quad (11)$$

and

$$\psi^* = V_0^* - (z/z_0)V_1^*. \quad (12)$$

The field strength \mathcal{E}_1^* is constant in the region $0 \leq z \leq z_0$.

Next, we must consider the effects of dielectric saturation in the charge-free layer. We shall choose equations for the dependence of ϵ_1 and κ_1 on \mathcal{E}_1^* of the same form as those used for these quantities in the diffuse layer. However, since the charge-free layer may have properties different from those of the solvent, the constants which enter the saturation equations must be taken different from those of the diffuse layer for generality. Even when the charge-free layer does consist of solvent material (perhaps only one or two molecules thick), one would not necessarily expect that the saturation and other constants of the material on such a microscopic scale should be equal to the corresponding constants of the bulk material. The equations therefore are

$$\kappa_1 = c_1 + a_1 [1 + 2b_1^* \mathcal{E}_1^{*2}]^{-1/2}, \quad (13)$$

and

$$\epsilon_1 = c_1 + a_1 [(2b_1^*)^{1/2} \mathcal{E}_1^*]^{-1} \sinh^{-1} [(2b_1^*)^{1/2} \mathcal{E}_1^*]. \quad (14)$$

Thus,

$$\kappa_1^0 = \epsilon_1^0 = c_1 + a_1.$$

Finally, we must consider the possibility that a high electric field strength in the charge-free layer can cause compression of this layer. In an aqueous electrolyte, one might expect the thickness of the charge-free layer to be the sum of the ionic radius of the ion attracted to the electrode plus the diameter of one or more water molecules if the ion is hydrated. If the force between ion and electrode is made sufficiently great, any water molecules present between the two will be flattened, and the shape of the ion itself may be somewhat distorted. Such compression might be expected to be linear for relatively small pressures with a gradual transition to a much smaller dependence on pressure for higher pressures.

We shall choose the following heuristic expression to represent the dependence of the thickness of the

charge-free layer on pressure applied to it:

$$z_0/z_0^0 = [1 + \beta p]^{-1}, \tag{15}$$

where β is a constant and z_0^0 is the value of z_0 for $V_0^* = 0$. Note that in the present one-dimensional treatment no distinction need be made between force and pressure. The above expression is linear for $\beta p \ll 1$, yet an infinite pressure is required to reduce z_0 to zero. Equation (15) should be a good approximation for small pressures, but it certainly cannot be expected to represent the behavior of real materials very accurately at high pressures such as those present in the charge-free layer when a relatively large negative polarizing potential is applied. Greater accuracy might be obtained by using a more sophisticated equation of state applicable to the actual material of the charge-free layer. Nevertheless, we shall see later that the above simple expression actually seems to describe the behavior of the charge-free layer quite accurately for aqueous electrolytes. The use of a more complicated expression is therefore not justified at present.

The electrostrictive pressure in the material is, from electrostatic theory,⁶

$$p = \epsilon_1 \mathcal{E}_1^2 / 8\pi. \tag{16}$$

We may now rewrite Eq. (15) as

$$z_0/z_0^0 = [1 + (\beta/8\pi)\epsilon_1 \mathcal{E}_1^2]^{-1} = [1 + \alpha \epsilon_1 \mathcal{E}_1^2]^{-1} = [1 + \alpha^* \epsilon_1 \mathcal{E}_1^{*2}]^{-1}, \tag{17}$$

where $\alpha = \beta/8\pi$ is another constant. This equation is more formidable than it appears, since ϵ_1 is also a function of \mathcal{E}_1 as shown by (14). We shall neglect any direct dependence of ϵ_1 and κ_1 on pressure since this effect can be at least partly included together with their dependence on the field \mathcal{E}_1 which produces the pressure.

Finally, it will be useful to derive the initial isothermal modulus of linear compressibility δ^0 from (15). Since $\delta^0 = - (z_0^0)^{-1} (\partial z_0 / \partial p)_T$ evaluated at $p = 0$, we find

$$\delta^0 = \beta = 8\pi\alpha. \tag{18}$$

Since α can be obtained by fitting experimental results with the theory, δ^0 may also be obtained.

JOINING CONDITIONS AT $z = z_0$

Since we have specified that there be no discontinuity in potential across the plane $z = z_0$, the principal additional condition which must be satisfied there is that the normal component of the electric displacement be continuous. In this one-dimensional treatment, this is the only component present and we obtain

$$D_1^* = D_2^*, \tag{19}$$

or

$$w \equiv (2b_1^*)^{1/2} \mathcal{E}_1^* \epsilon_1 = (2b_1^*)^{1/2} \mathcal{E}_2^* \epsilon_2 = (b_1^*/b_2^*)^{1/2} \epsilon_2 u.$$

⁶L. Page and N. I. Adams, *Principles of Electricity* (D. Van Nostrand Company, Inc., New York, 1949), second edition, p. 50.

This may be written as

$$w = (b_1^*/b_2^*)^{1/2} [c_2 u + a_2 \sinh^{-1} u], \tag{20}$$

using Eqs. (4) and (7). We thus see that if \mathcal{E}_1^* is specified, w may be computed using (14) and u determined from a graph of w versus u . We can then calculate V_2^* , as discussed previously, and can obtain V_1^* from (11) if z_0 is known. From $V_0^* = V_1^* + V_2^*$, we can finally obtain the applied potential which would result in the value of \mathcal{E}_1^* originally assumed. This appears to be a complicated procedure but, since most of the quantities in which we are interested are implicit functions of each other, it seems to be the simplest possible method.

THE DIFFERENTIAL CAPACITANCE FORMULA

The introduction of dielectric saturation in both layers and compression of the first layer complicates the calculation of the total differential capacitance. It may be obtained from any of the following equivalent equations

$$C_T^d = \frac{d\sigma_m^*}{dV_0^*} = \frac{d\sigma_m^*}{d\mathcal{E}_2^*} \frac{d\mathcal{E}_2^*}{dV_2^*} \frac{dV_2^*}{dV_0^*} = \frac{d\sigma_m^*}{d\mathcal{E}_1^*} \frac{d\mathcal{E}_1^*}{dV_0^*}. \tag{21}$$

Here, σ_m^* is the normalized charge density on the metal electrode. We shall use the last of these expressions since it turns out to be the simplest to apply. We shall now calculate the factors in this expression separately. The first is readily obtained from Gauss' law, $D^* = 4\pi \times L_D^0 \sigma_m^*$, written in terms of normalized variables. On differentiating this equation with respect to \mathcal{E}_1^* and using the definition of κ_1 we find

$$\frac{d\sigma_m^*}{d\mathcal{E}_1^*} = \frac{\kappa_1}{4\pi L_D^0}. \tag{22}$$

The calculation of $(d\mathcal{E}_1^*/dV_0^*)$ is considerably more difficult. If we take $z = z_0$ in (12) and differentiate with respect to \mathcal{E}_1^* , using $V_0^* = V_1^* + V_2^*$ and (11), we obtain

$$\left(\frac{d\mathcal{E}_1^*}{dV_0^*} \right)^{-1} = \frac{d\psi^*}{d\mathcal{E}_1^*} + z_0 + \mathcal{E}_1^* \frac{dz_0}{d\mathcal{E}_1^*}. \tag{23}$$

The last term may be calculated from (17) using (2). We obtain

$$\mathcal{E}_1^* \frac{dz_0}{d\mathcal{E}_1^*} = \left(1 + \frac{\kappa_1}{\epsilon_1} \right) (z_0 - z_0^0) (z_0/z_0^0). \tag{24}$$

Further, we find from (19) that at $z = z_0$

$$\frac{d\psi^*}{d\mathcal{E}_1^*} = \frac{\kappa_1}{\kappa_2} \frac{d\psi^*}{d\mathcal{E}_2^*}. \tag{25}$$

Equation (5) may be rewritten as

$$\frac{d^2\psi^*}{dz^2} = -\mathcal{G}^* \frac{d\mathcal{E}^*}{d\psi^*} = -\epsilon_2^0 \rho^* / \kappa. \tag{26}$$

If we now substitute (1) in (26) and evaluate the result in the diffuse layer at $z=z_0$, we finally obtain

$$\frac{d\psi^*}{d\mathcal{E}_2^*} = \frac{\kappa_2}{\epsilon_2^0} \frac{\mathcal{E}_2^*}{\sinh V_2^*}. \quad (27)$$

These results may now be substituted in Eq. (21) to yield the following formula for C_T^d

$$C_T^d = C_1^0 \left[\left(\frac{\kappa_1^0}{\kappa_1} + \frac{\epsilon_1^0}{\epsilon_1} \right) \left(\frac{z_0}{z_0^0} \right)^2 - \frac{\epsilon_1^0}{\epsilon_1} \left(\frac{z_0}{z_0^0} \right) + \gamma \mathcal{E}_2^* (\sinh V_2^*)^{-1} \right]^{-1}, \quad (28)$$

where

$$\gamma \equiv \kappa_1^0 / (\kappa_2^0 z_0^0) = (\kappa_1^0 L_D^0) / (\kappa_2^0 x_0^0) \quad (29)$$

and

$$C_1^0 \equiv \kappa_1^0 / (4\pi x_0^0). \quad (30)$$

The quantity C_1^0 is the differential (and static) capacitance of the first layer alone with $V_0^*=0$. Similarly, the corresponding capacitance of the diffuse layer for $V_0^*=0$, C_2^0 , may be obtained from

$$C_2^0 = (d\sigma_m^* / dV_2^*)_{V_0^*=0}$$

and Eqs. (19), (22), and (27), together with the limiting result that $\mathcal{E}_2^* / \sinh V_2^* = 1$ at $V_0^*=0$. This result itself follows directly from Eq. (6). We finally obtain

$$C_2^0 \equiv \kappa_2^0 / (4\pi L_D^0). \quad (31)$$

We thus note that $\gamma = C_1^0 / C_2^0$ and that Eq. (28) yields the usual expression for these two capacitances in series at $V_0^*=0$. In the opposite limit of very high applied potentials, Eq. (6) shows that $\mathcal{E}_2^* / \sinh V_2^*$ approaches zero, so that C_T^d approaches

$$C_1^0 \left[\left(\frac{\kappa_1^0}{\kappa_1} + \frac{\epsilon_1^0}{\epsilon_1} \right) \left(\frac{z_0^\infty}{z_0^0} \right)^2 - \left(\frac{\epsilon_1^0}{\epsilon_1} \right) \left(\frac{z_0^\infty}{z_0^0} \right) \right]^{-1},$$

which may considerably exceed C_1^0 if $z_0^\infty \ll z_0^0$. Equation (28) is independent of the sign of V_0^* since \mathcal{E}_2^* and V_2^* will always have the same sign. Although the method of obtaining Eq. (28) is completely general, the equation itself applies only to the case where z_0/z_0^0 is given by (17).

The use of Eq. (28) to calculate C_T^d for a given value of V_0^* is not completely straightforward even when all the constants are known because of the implicit relations between the various variables. In practice such calculation can be carried out most simply by first calculating the values of κ_1 , ϵ_1 , and w corresponding to an initially selected value of \mathcal{E}_1^* . The quantity u is then determined from a graph of w versus u and this value of u entered in a graph of η versus u to yield the corresponding value of η . Then, V_2^* can be calculated from Eq. (10). Next, after calculating z_0 from (17), V_1^* can be obtained using (11). The normalized applied potential $V_0^* = V_1^* + V_2^*$ corresponding to the selected value of \mathcal{E}_1^* is thus

finally obtained and the value of C_T^d corresponding to this potential obtained from (28), all of whose factors are now known.

There are, unfortunately, a number of constants entering the theory which will not be known independently of measurements of C_T^d versus V_0 . Thus, in order to fit the theoretical curves to such data, the constants will have to be derived from the data. Luckily, most of the constants are independent of each other. First, $\kappa_2^0 = \epsilon_2^0$ is just the normal dielectric constant of the solution; for aqueous solutions, it will be that of water at the given temperature with possibly a small correction for solute concentration at high concentrations. The quantity $c_2 = \kappa_2^\infty$ is the nonpolar part of the dielectric constant of the diffuse layer remaining after the polar contribution is saturated by a high electric field. It may be approximately inferred from the optical index of refraction. Since the frequency at which differential capacitance measurements are commonly carried out is less than 10^6 cps, the use of n^2 for c_2 represents a hazardous extrapolation. Hasted and El Sabeh⁷ quote a figure of 4 for the far infrared dielectric constant of water. From their measurements on water at wavelengths between 1 and 10 cm, however, they find a high-frequency limiting dielectric constant ϵ_∞ of 5.2 ± 0.5 at 20° and 30°C . This latter figure should at least approximately represent the dielectric constant of water after the polar contribution is entirely relaxed. We shall therefore choose the value $c_2 = 5$ for the diffuse layer. In addition, since evidence to be presented later derived from the experimental data on NaF indicates that the charge-free layer itself consists of water molecules, we shall take the same value for c_1 and let $c_1 = c_2 = c = 5$. The lack of a more precise value for c will not affect most of our conclusions appreciably.

Luckily, it is possible to obtain the ratio κ_1^0/x_0^0 in an unambiguous way from measurements of C_T^d at $V_0^*=0$ for various concentrations.⁸ This is the case because the constants α and b which control compression and saturation arising from the applied field have no effect on the value of C_T^d at $V_0^*=0$. Further, κ_1^0/x_0^0 is essentially independent of concentration in NaF and other electrolytes which show no specific absorption. After the determination of κ_1^0/x_0^0 , κ_1^0 can be determined either from an independently known value of x_0^0 , or can be found from detailed curve fitting. In the latter case, x_0^0 is itself determined. Finally, the constants a_1 , b_1 , b_2 , and α must be found from a fit of the experimental curve of C_T^d versus V_0 for a given concentration. A check of the resulting values can then be made by using the same values to compute the theoretical dependence of C_T^d on V_0 for another concentration for comparison with experimental results. The agreement between theory and experiment should be good for

⁷ J. B. Hasted and S. H. M. El Sabeh, *Trans. Faraday Soc.* **49**, 1003 (1953).

⁸ J. R. Macdonald, *J. Chem. Phys.* **22**, 763 (1954).

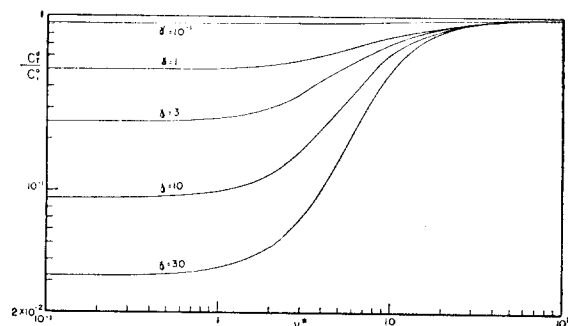


FIG. 2. Dependence of normalized differential capacitance on normalized potential for different values of $\gamma = C_1^0/C_2^0$ with no dielectric saturation and no compression.

the new concentration for a correct initial choice of the constants.

When $\alpha = b_1 = b_2 = 0$, the formula for C_T^d and its calculation for various values of V_0^* is greatly simplified. The capacitance of the initial charge-free layer is then C_1^0 and is independent of applied potential. This capacitance is in series with the normal differential capacitance of the diffuse layer without dielectric saturation, C_2^d . This capacitance is nonlinear and depends strongly on V_0^* . Curves showing the dependence of the total capacitance C_T^d on V_0^* for this situation are presented in Fig. 2, with γ as a parameter. The shape of these curves is readily explained. When γ is large, C_1^0 is much larger than C_2^0 . Thus, C_2^0 determines the value of C_T^d for $V_0^* < 1$. However, as V_0^* increases, C_2^d increases until it is much larger than C_1^0 , which itself then determines C_T^d . On the other hand, when $\gamma \ll 1$, C_2^d is much larger than C_1^0 for all values of V_0^* , so that C_T^d is essentially independent of V_0^* . Note that at 25°C, a value of 10 for V_0^* corresponds to an applied potential of about 0.26 volt; thus, saturation of these curves occurs at low potentials.

COMPARISON WITH EXPERIMENT

In this section, we shall compare the predictions of the theory with experimental data on NaF for various concentrations at 25°C. These data were obtained by D. C. Grahame,⁹ who has found that NaF shows little or no specific adsorption on negative polarization. Although the theory indicates that the shape of the C_T^d versus V_0 curves should be symmetric about $V_0 = 0$, the experimental curve shape for $V_0 > 0$ differs from that for $V_0 < 0$ even for NaF. The lower the concentration, the larger the range of $|V_0|$ about zero over which the symmetry is preserved, but even at 0.001N deviations between the two halves begin to appear for $|V_0| \gtrsim 0.2$ volt. It is probable that the large increase in C_T^d observed with strong positive polarization arises from specific adsorption of the highly polar-

izable anions. Since we present theory does not include adsorption effects, we shall restrict attention to data for which $V_0 < 0$.

The first step in the curve-fitting is the calculation of κ_1^0/x_0^0 . We take κ_2^0 and ϵ_2^0 as 78.5, the value for water at 25°C.¹⁰ We shall neglect the small concentration dependence of these quantities. After calculating L_D^0 for the various concentrations, C_2^0 can be computed from theory. Finally, C_1^0 can be obtained from the experimental values of C_T^d at $V_0 = 0$ and the values of C_2^0 . Then γ can be calculated for each concentration. The resulting values of κ_1^0/x_0^0 are shown in Table I. Since κ_1^0/x_0^0 is determined from the difference of two large numbers for low concentrations, the resulting values are inaccurate. The value of κ_1^0/x_0^0 is essentially constant for concentrations of 0.1N and higher; thus, we have averaged the last three values in the table to obtain the value $\kappa_1^0/x_0^0 = 3.257 \times 10^8 \text{ cm}^{-1}$, which may be presumed to be independent of concentration. The corresponding value of C_1^0 is 28.9 $\mu\text{f}/\text{cm}^2$. We have used this average value of κ_1^0/x_0^0 in the computation of the γ 's which also appear in Table I.

We now have sufficient information to compare the theoretical curves for the various γ 's with the experimental results, provided that we take $\alpha = b_1 = b_2 = 0$. Such comparison is presented in Fig. 3. The curve for 0.660N is omitted since it is similar to that for 0.916N and lies too close to it for clarity of presentation. Two conclusions may be drawn from this graph; first, that agreement between theory and experiment is satisfying for very low potentials near $V_0 = 0$; and second, that the deviations between theory and experiment begin to occur at lower and lower potentials the higher the concentration. It is worth noting that the agreement indicated in Fig. 3 is based on the use of only a single constant, κ_1^0/x_0^0 , derived from the experimental results.

In the preceding theoretical development, we have introduced the saturation constants b_1 and b_2 , which are, in general, unequal. For the present comparison with experiment, however, it turns out that although there is appreciable saturation in the diffuse layer with a large polarizing potential applied, such saturation has only a very small effect on C_T^d .^{2,9} The reason for this behavior is that when the potential across the diffuse layer is sufficiently large to produce saturation, it is also large enough to increase the capacitance of this layer to the point where it no longer has much effect on the total capacitance C_T^d . Thus, the value of b_2 chosen will have little effect on the shape of the

TABLE I. Dependence of κ_1^0/x_0^0 and $\gamma (= C_1^0/C_2^0)$ on concentration for NaF at 25°C.

Normality:	10^{-3}	10^{-2}	10^{-1}	0.660	0.916
$\kappa_1^0/x_0^0(\text{cm}^{-1})$:	$3.79 \cdot 10^8$	$3.39 \cdot 10^8$	$3.268 \cdot 10^8$	$3.241 \cdot 10^8$	$3.293 \cdot 10^8$
γ :	3.97	1.26	0.397	0.155	0.131

⁹ D. C. Grahame (private communication). To be published in J. Am. Chem. Soc. Also available from D. C. Grahame, Amherst College, as O.N.R. Report No. 14, 18 February, 1954.

¹⁰ Dorsey, *Properties of Ordinary Water-Substance* (Reinhold Publishing Corporation, New York, 1940), p. 367.

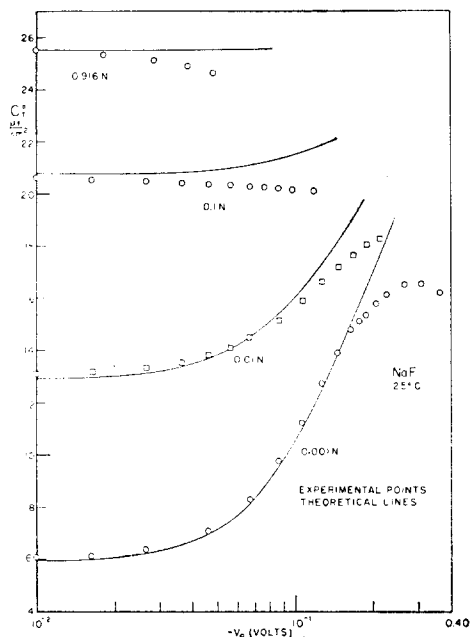


FIG. 3. Comparison of theory without dielectric saturation and compression with experimental data on NaF at 25°C.

C_T^d curves, and b_2 cannot therefore be obtained even as to order of magnitude from C_T^d data. Since there is evidence that the charge-free layer consists of water, one might expect that b_1 would equal b_2 unless local conditions near the boundary should preferentially affect b_1 . We shall therefore choose $b_1 = b_2 = b$. The value of b derived from the data will thus apply to the charge-free layer and will be only slightly affected by any difference between b_1 and b_2 . While it would be possible to take $b_2 = 0$ with less than a percent change in the theoretical curves, it seems preferable to include its small effect as above, especially since it is possible to obtain agreement between theory and experiment to better than two percent when the assumption that b_1 is equal to b_2 is made.

Next, we shall discuss the determination of the constants κ_1^0 , α , and b , and the fitting of complete C_T^d curves for negative polarization. It is possible to obtain an approximate value of κ_1^0 from the expected value of x_0^0 based on the assumption that only a single water molecule lies between the metallic electrode and each of the nearest positive ions. This assumption yields a value of x_0^0 of 4.4 Å, made up of about 1.0 Å, the radius of a Na^+ ion,¹¹ and 3.4 Å, the approximate diameter of a water molecule.¹² These figures and the result for x_0^0 are quite approximate because of the difficulty of attaching a precise meaning to the diameters of contiguous ions and molecules in solution. In spite of possible inaccuracy, the figure 4.4 Å furnishes a starting

¹¹ C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), p. 40.

¹² N. K. Adam, *The Physics and Chemistry of Surfaces* (Oxford University Press, London, 1941), third edition, p. 125.

point for our calculations and leads to a value of about 14 for κ_1^0 .

Initially, however, a value of κ_1^0 of 78.5 was used in fitting the experimental curve for 0.01N in order to see if a good fit could be achieved for this value and to see to what consequences such a value would lead. It was found that the experimental curve could indeed be fairly well fitted over its entire range provided that c was taken about 30. This large a value of the nonpolar contribution to the dielectric constant is exceedingly unlikely. Furthermore, the above value of κ_1^0 leads to $x_0^0 = 24$ Å, a value which would require many water molecules between electrode and the nearest positive ions. Since both of these results are very unlikely, it is obviously necessary to choose a smaller value of κ_1^0 , such as the value 14 considered above.

When the value $\kappa_1^0 = 14$ was employed together with $c = 5$, values of b and α could be found which would give a fair fit of the 0.01N C_T^d curve. However, slightly better agreement was found with $\kappa_1^0 = 15$, which still allows us to conceive of the charge-free layer as involving only a single water molecule since it yields a thickness of 4.6 Å for this layer. Figure 4 shows the results of such a curve fit. Theory and experiment agree to better than two percent over the full range of V_0 . Such agreement is, however, not very surprising when one remembers that we have used three or four adjustable constants in making the fit. Also shown on this graph are the curves for $\alpha = b = 0$ and for $\alpha = 0$ which show the individual effects of these constants. Since the best value of α has little effect on the curve near its maximum at about -0.26 volt, the initial determination of b can be carried out largely independent of knowledge of α . Then, after a good value of b has been obtained with the neglect of α , points near the high end of the curve may be used to obtain a good value of α . The

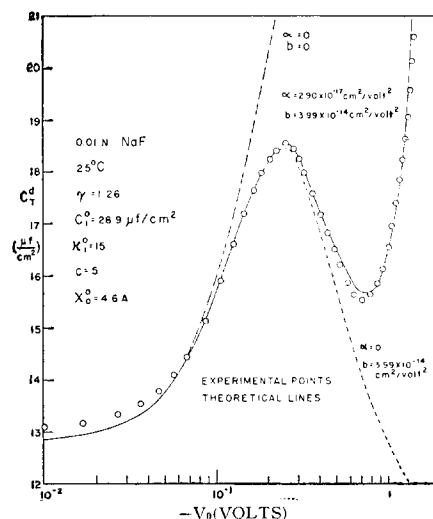


FIG. 4. Comparison of experimental data on 0.01N NaF at 25°C with theory for (a) no dielectric saturation, no compression ($\alpha = b = 0$), (b) no compression ($\alpha = 0$), and (c) both saturation and compression effects included.

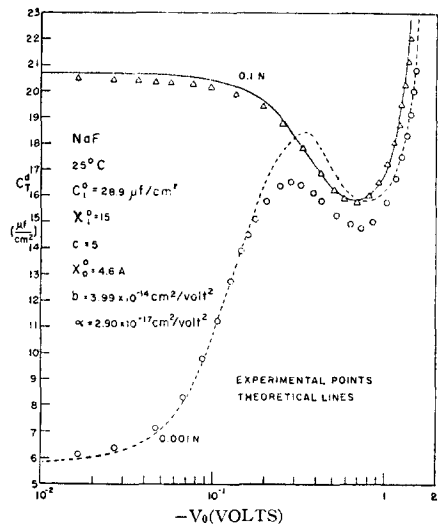


FIG. 5. Comparison of experimental data on 0.1 N and 0.001 N NaF at 25°C with theory using constants derived from 0.01 N data.

approximate independence between the effects of the two constants simplifies curve fitting greatly. It might also be mentioned that the choice of κ_1^0 has only a small effect on the value of b which allows the best fit between theory and experiment to be obtained.

The above results show that it is possible to obtain good agreement between theory and experiment for a single concentration by properly selecting several parameters. A much more stringent test of the theory is to use the parameters determined for one concentration to compute theoretical curves for comparison with experimental results for different concentrations. In Fig. 5, we show such results for 0.1N and 0.001N NaF at 25°C. The agreement between the theoretical line and the experimental points for 0.1N NaF is better than one percent over most of the range. At very small potentials, the difference is of the order of 1.5 percent. This small discrepancy (and the corresponding one for the 0.01N curve of Fig. 4) could have been reduced even further by different choices of γ . The value of γ used for each curve is that shown in Table I and is therefore that which is most consistent with the $V_0^* = 0$ data for all the other concentrations. The small discrepancy between the theoretical and experimental 0.1N curves at the highest negative polarizing potentials will be discussed later in connection with the value of α . When the constants derived from the 0.01N data are used to calculate curves for the higher concentrations above 0.1N, substantially as good agreement between theory and experiment is found as that shown for the 0.1N curve.

The discrepancy between theory and experiment for the 0.001N curve also shown in Fig. 5 requires special comment, however. The evidence of good agreement between theory and experiment for all other concentrations strongly suggests that the present discrepancy

arises from experimental error in the 0.001N data. Grahame⁹ has analyzed these same data by a method which involves the use of an experimentally determined curve of the dependence of the differential capacitance of the charge-free layer on polarizing potential, and has likewise obtained excellent agreement between his data and calculated curves except for the present case of 0.001N. In addition, his calculated curve for 0.001N is in good agreement with that of the present work in spite of a considerable difference in the methods of calculation. Grahame himself feels that the discrepancy arises from experimental error, which is most likely to occur at this lowest concentration. The consistent agreement between theory and experiment suggests that we can have considerable confidence in the applicability of the theory to the experimental situation found with negative polarization and no adsorption. Thus the saturation and other constants derived from curve fitting should be quite accurate and should describe some of the properties of the charge-free layer well. Next, we shall compare some of these constants with corresponding values for bulk water obtained from very different experiments. The resulting agreement or disagreement should allow a decision to be reached as to the nature of the charge-free layer.

First, we have found that good agreement between theory and experiment can be obtained with $c = 5$, a reasonable value for water. Even though such agreement is not strongly dependent on the value of c chosen, the above result is at least consistent with the supposition that the charge-free layer involves only a single molecule of water. The next result, $\kappa_1^0 = 15$, leads to a thickness for the layer again consistent with the single-molecule hypothesis. However, the value of 15 is about five times smaller than the value of the initial dielectric constant of bulk water. If this reduction were ascribed to an initial partial saturation of the layer dielectric constant by the inhomogeneous image-charge field of the nearest ion even in the absence of an applied potential, one would expect to find κ_1^0 considerably less than ϵ_1^0 . On the contrary, however, the degree of agreement between the data and theory shown in Fig. 3 for potentials sufficiently small that the effect of b is still negligible can only be obtained if κ_1^0 and ϵ_1^0 are taken substantially equal. We are thus left with the possibilities that the principal material of the charge-free layer is either not water or that some of its properties are different from those of ordinary bulk water. If the charge-free layer consists of a single water molecule and half of a sodium ion, as the thickness result suggests, the initial dielectric constant of the layer could perhaps be less than that of ordinary water either because the water molecule was not surrounded by the usual number of neighboring water molecules and/or possibly because the effective dielectric constant of the layer was some kind of complicated average of the dielectric constant of a single water molecule and that of the part of the sodium ion between its center of

charge and the water molecule. In view of the conceptual difficulty in attaching a precise meaning to the dielectric constants of these microscopic entities, the discrepancy between the effective value of 15 and that of bulk water should not be weighted heavily in deciding whether the ion nearest the polarized electrode is indeed hydrated.

Next, we may compare the value of b of 3.99×10^{-14} cm²/volt² obtained from the curve-fitting with that obtained for water by other methods. Malsch^{2,13} found $b = 1.2 \times 10^{-13}$ cm²/volt² by direct measurement of the differential dielectric constant of water up to applied fields of the order of 2.5×10^6 volts/cm. At these fields κ would be reduced from its initial value by less than one percent by using Malsch's own value of b . Thus his result cannot be expected to be very accurate, and it is possible that our value, which is three times smaller, is the more accurate if it indeed applies to water. Since the present work shows that the field \mathcal{E}_1 in the charge-free layer can reach values as large as 3×10^7 volts/cm, one would expect very strong saturation effects to occur in this layer. The order of magnitude of these effects can be seen by comparing the various curves in Fig. 4. Thus the present method of obtaining b does not suffer from the disadvantage of deriving it from data for which its effect is very small, and the resulting value of b is hence probably quite accurate. Since the value of b obtained applies to a very small amount of material, however, it may be unreasonable to expect this value to be the same as that of the material in bulk. If b is the saturation constant of a single water molecule, either this constant is approximately the same as that of bulk water, in which case Malsch's result is somewhat in error, or else both values are approximately correct and the saturation constant for a single molecule of water is less than that for bulk water. Further direct measurements of κ to higher field strengths than Malsch employed will be required to decide between these possibilities. Nevertheless, the arrangement to order of magnitude between Malsch's result and that of the present work again affords strong evidence that the ion nearest the electrode is hydrated.*

Finally we shall investigate what information may be obtained from the experimentally derived value of

¹³ F. Malsch, *Physik Z.* **29**, 770 (1928); **30**, 837 (1929).

* *Note added in proof.*—I wish to thank Professor D. C. Grahame for pointing out that since any direct pressure dependence of the dielectric constant is included herein with its dependence on electric field strength, the value of b determined from electrolyte data may not be directly comparable with that from Malsch's experiment. Since the dielectric saturation in both kinds of experiment arises from an electric field which produces an electrostrictive pressure in the material, this pressure will be the same in either experiment for a given field strength. Thus, Malsch's determination of b must also tacitly include a pressure effect in the resulting value of b . However, since the pressure may act differently on a single water molecule in the charge-free layer than on bulk water, the direct pressure contribution to b may differ in the two cases and perhaps accounts for some or all of the discrepancy between the b values.

α of 2.90×10^{-17} cm²/volt². Now if the units of α are converted to those of an inverse pressure, α becomes 2.61×10^{-12} cm²/dyne. Next we may use Eq. (18) to obtain the effective linear compression modulus of the charge-free layer. The result is $\delta^0 = 6.56 \times 10^{-11}$ cm²/dyne. There are no results available for the linear compressibility of bulk water since water is a liquid. We can make a rough comparison, however, between the above value and the volume compressibility of bulk water. First, it will be of interest to inquire how well bulk water volume follows a law of the form (15) with z_0/z_0^0 replaced by v/v_0 . We calculate $(v_0/v - 1)$ by using Bridgman's data for water¹⁴ and plot this quantity *versus* pressure on a log-log graph. If an equation of the form (15) is well satisfied, we should obtain a straight line of slope unity. It is actually found that such a procedure yields a straight line of unity slope only for pressures up to about 10^3 atmospheres and that thereafter there is a transition to a slope of about 0.7 up to 10^4 atmospheres. From the low pressure region, we can obtain a value for the initial compressibility modulus k^0 . Interpolating Bridgman's data for 20° and 30°C, we find

$$k^0 \cong 4.2 \times 10^{-11} \text{ cm}^2/\text{dyne at } 25^\circ\text{C.}$$

In an isotropic solid, k^0 should be three times larger than δ^0 . Our value for δ^0 is, however, almost five times larger than $k^0/3$ for bulk water. Since it is patently impossible to consider a single water molecule as an isotropic solid, the above difference is not surprising, and the degree of agreement between the value of k^0 for bulk water and the present value of δ^0 is strong evidence that a water molecule is being compressed in the charge-free layer. The result that δ^0 is slightly larger than k^0 may be evidence that the water molecule can belly out to the sides rather freely under linear compression as one might expect. If we consider the charge-free layer to consist of a single water molecule plus that part of a sodium ion between its center of charge and the water molecule, compression of the water molecule must be accompanied by some compression of the sodium ion as well. Since the bulk compressibility of sodium is about five times smaller than our value for the linear compressibility of the entire charge-free layer, we shall probably make only a small error by neglecting any compression of the sodium.

If the linear compression of a water molecule has a dependence on pressure of roughly the same form as does the volume compression for bulk water, then Bridgman's data indicates that Eq. (15) can only be expected to apply well for relatively low pressures and that for high pressures compression should occur less rapidly with increasing pressure than predicted by (15). Now a pressure of 10^3 atmospheres is reached in the charge-free layer at a bias potential of about -0.7 volt for a concentration of 0.01N; and at -1.4 volts the

¹⁴ *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1928), Vol. 3, p. 40.

pressure is of the order of 4×10^3 atmospheres or greater. Therefore, we may expect (15) to be a poorer and poorer approximation for polarizing potentials more negative than about -0.7 volt. The theory would thus predict a more rapid compression and consequent rise in C_T^d than would be observed experimentally for numerically larger polarizing potentials than -0.7 volt. Some such tendency is actually observed for all the curves, since near the largest negative polarizing potentials the theoretical lines rise slightly faster than the experimental points for all concentrations. It might be noted that the maximum compression of the charge-free layer leads to only about a 20-percent decrease in the thickness of the layer. It is certainly not unreasonable to imagine that a water molecule could be compressed by this amount by the very high pressure present in the layer.

The effect of temperature on the theoretical curves is rather complex. Since there are no data available showing temperature dependence for a constant concentration in electrolytes with no adsorption, we shall only discuss this matter qualitatively. If we assume that x_0^0 and the dielectric parameters are relatively independent of temperature in the range considered, an increase in temperature will increase L_D^0 and γ in the same fashion as would a decrease in concentration. At the same time, z_0^0 will decrease while b^* and α^* will increase if b and α remain constant. Finally, for fixed V_0^* , a temperature increase will increase V_0 , stretching the potential scale. These various changes partly cancel out of the curve of C_T^d versus V_0 . Thus an increase from 25°C to 75°C is found to decrease the theoretical value of C_T^d at $V_0 = -0.4$ volt by only about three percent for 0.001N concentration.

CONCLUSIONS

In spite of the approximate character of those assumptions of the theory involving dielectric saturation and compression and the use of a one-dimensional approximation to represent a truly two-dimensional problem, good agreement has been found between the predictions of the theory and experiment in respect to the dependence of the differential capacitance on negative polarizing potential and on concentration.

The agreement between theory and experiment is especially satisfying since it is obtained using the same values of the constants c , κ_1^0 , x_0^0 , b , and α for all concentrations. Since these quantities describe properties of the charge-free layer, one would not expect them to depend on electrolyte concentration in the bulk of the system.

The following results are consistent with the assumption that the charge-free layer involves a single molecule of water so that positive ions nearest the negative electrode are hydrated: (a) The nonpolar part of the dielectric constant of the charge-free layer is 5. (b) The initial thickness of the charge-free layer is 4.6 Å, made up of about 1 Å, the radius of a Na^+ ion, and 3.6 Å, the diameter of a water molecule. (c) The dielectric saturation constant of 3.99×10^{-4} cm²/volt² is three times smaller than the approximate value obtained by Malsch for bulk water using direct methods but relatively low field strengths. (d) The initial linear isothermal compressibility modulus of the charge-free layer is 50 percent larger than the initial volume compressibility of bulk water. The maximum pressure in the charge-free layer of 4×10^4 atmospheres or greater results in a reduction in thickness of the layer of about 20 percent.

The complete theory applies not only to aqueous electrolytes, but also to any solid or liquid polar materials containing mobile positive and negative univalent ions blocked at an electrode. It may be readily generalized to include the case of ions of higher valency. Without the refinements of dielectric saturation and compression of the charge-free layer, the theory describes the behavior for reverse bias of nonpolar rectifiers with intrinsic conduction which contain an insulating film between the metallic electrode and the bulk of the material.

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