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DIFFERENTIAL CAPACITY AND STRUCTURE OF THE ELECTRICAL DOUBLE LAYER AT THE MERCURY/ELECTROLYTE INTERFACE

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1. INTRODUCTION

It is well known that an electrical double layer appears at the interface between two phases, one of which contains ions or polar molecules; it is formed because the electrochemical potentials in the two phases (*e.g.* metal and solution) are unequal. In general, one needs to consider the difference in chemical potential for the ions in the metal and in the solution, the influence of any external electric field, and also the specific adsorption of ions or polar molecules on the metal surface.

If any of the components of a system comprising an electrode immersed in an electrolyte is present in both phases at finite concentrations, an electrochemical reaction may be made to proceed in either direction by an externally applied potential. It is usually assumed that equilibrium in the electrical double layer is not thereby disturbed, and that the passage of current through the electrode/solution interface affects the double layer structure only in so far as it alters the surface concentration of ions. Levich has discussed[1,2] the non-equilibrium double

layer. Equilibrium in the electrical double layer is maintained also when a low-amplitude alternating current is passed through the electrode, provided the frequency is not too high. However, the impedance measured by an alternating current is found[3-8] to be a complex quantity when an electrochemical reaction is proceeding at the metal surface, and there is no easy method of applying such measurements to the problem of establishing the structure of the double layer. Therefore, in studies of the double layer structure in the presence of various inorganic and organic materials, it is usual to employ an ideally polarisable electrode, *i.e.* an electrode such that the passage of ions through the interphase boundary is either thermodynamically impossible or very strongly retarded by a high energy of activation. A system consisting of mercury and a deoxygenated solution of a capillary-inactive electrolyte (*e.g.* KCl) approximates to an electrode of this type over a certain range of potential. This paper is concerned, on the whole, with electrodes which are similar in properties to the ideally polarisable electrode.

The ideally polarisable electrode is the site of an electrostatic equilibrium between two phases and is therefore electrically equivalent to a leakage-free capacitor. The thermodynamic considerations connecting the interfacial tension (σ) between a metal and a solution with the charge (ϵ) and potential (φ) of the electrode, and with the surface density and the activity of ions and molecules in the dissolved state (Γ_i and a_i respectively), are applicable to the ideally polarisable electrode. The thermodynamic treatment of this electrode leads to the basic equation of electrocapillarity, which may be expressed in the following form at constant temperature and pressure:

$$d\sigma = -\epsilon d\varphi - \sum_i RT\ \Gamma_i\ d\ln a_i, \qquad (1)$$

where R is the gas constant and T the absolute temperature. This equation was first derived by Frumkin[9] on the assumption that potential-determining ions were present in solution; the derivation is strict and is equally applicable to electrodes which are not ideally polarisable (*e.g.* thallium amalgam[10,11]). However, Frumkin's argument met with criticism as regards the ideally polarisable electrode, as it did not correspond to physical reality. Numerous alternative derivations of the electrocapillarity equation have since been put forward[12-14], but they all lead to the same result. A detailed study of the thermodynamics of adsorption at the electrode/solution interface has recently been carried out by Parsons[15].

The basic electrocapillarity equation leads to some important conclusions on the adsorbability of ions and neutral molecules at an electrode surface. In particular, Lippman's equation, which relates the differential capacity of the electrical double layer (C) to the surface tension, follows directly from Eqn. (1) when the solution composition constant is:

$$C = \frac{d\epsilon}{d\varphi} = -\frac{d^2\sigma}{d\varphi^2}. \qquad (2)$$

There are two main methods of studying the electrical double layer at an ideally polarisable electrode: the electrocapillarity curve method, developed by Gouy[16-18] and by Frumkin[19], and the method based on measurements of differential capacity. Although the earliest direct measurements of double layer capacity were carried out as long ago as 1870 by Varley[20], all the measurements reported up to 1935 gave differential capacity values several times smaller[21-26] than those calculated on the basis of Eqn. (2) using the second differential of the electrocapillarity curve. This inconsistency was resolved in 1935 by Proskurnin and Frumkin[27], who showed that the double layer capacity was extremely sensitive to traces of organic impurities and that reliable values for differential capacities could be obtained only if the experiments were conducted under the most stringent conditions of cleanliness (such as careful purification of all reagents to remove organic impurities and the use of apparatus containing no rubber tubing or bungs or greased joints).

When comparing the relative merits of the electrocapillary curves and the differential capacity curves it should be remembered that the capacity is more sensitive to changes in the double layer structure than is the surface tension. Thus, differential capacity curves are sensitive to the minutest traces of surface-active substances in solution. The capacity at φ = -0.7 V (normal calomel electrode) is lowered by $\sim 4\ \mu F\ cm^{-2}$ for 3 N KCl when n-butyl alcohol is added to the 6×10^{-3} M level[28], but the surface tension is changed[29] by no more than 0.7 dyne cm^{-1} (these quantities can be measured with a precision of $\sim 1\%$ and $\sim 10\%$ respectively). On the other hand, the information on the electrical double layer which the differential capacity curves can provide is less complete than that derived from electrocapillarity measurements. In practice, the evaluation of surface charge and ionic adsorption from differential capacity data involves integration constants which need to be determined independently, as will be shown below. Electrocapillarity measurements are particularly suitable in this respect. If follows that the two methods (differential capacity and electrocapillary curves) must in general be considered as complementing each other in double layer studies. With solid electrodes, which do not permit direct electrocapillarity measurements, only the differential capacity method is available. Numerous recent papers deal with measurements of the differential capacity of solid electrodes[30-46], but this work suffers from experimental difficulties inherent in the preparation of clean, smooth, and reproducible surfaces, and therefore lacks precision. This is the reason for the choice of the mercury electrode in studying the structure of the double layer. We shall therefore confine this discussion, on the whole, to measurements carried out at the mercury electrode. The limited data which have been published about the surface tension[47] and the differential capacity[48] of the liquid gallium electrode are entirely in keeping with what is known about the mercury electrode.

Since present-day views on the nature of the electrical double layer are so largely based on measurements of differential capacity, we discuss briefly the relevant techniques.

2. METHODS FOR MEASURING DIFFERENTIAL CAPACITY

The current literature offers a remarkable choice of methods for measuring differential capacity. These may be tentatively classified into two groups: pulse methods and a.c. methods, the latter relying on the use of sinusoidal alternating current.

The first group includes the fast surface-charging method, due to Bowden and Rideal[24], whereby the double layer capacitance is computed from charging curves recorded on an oscillograph (see also ref.21). This method has recently been improved by Brodd, Hackermann, and

McMullen[46,49], who used square-wave pulses for charging the surface. Loveland and Elving's method[50], in which a triangular waveform is applied to the (ideally polarisable) electrode and the capacitative current is displayed on an oscilloscope, also belongs to the first group. When the resistance of the electrolyte is low, the current is proportional to the capacitance of the double layer, so that the two symmetrical differential capacity curves (corresponding to the leading and the trailing edge of the triangular pulse) which appear simultaneously on the oscilloscope involve the charging and the discharging current respectively. Finally, the commutator method developed by Borisova and Proskurnin[51] should be included among the pulse techniques. This method consists in connecting the test electrode and a standard capacitor in turn to a charged condenser, and measuring the amplified potential difference with the help of a ballistic galvanometer. The throws obtained with the test electrode and the standard capacity are inversely proportional to their capacities. The main advantage of the commutator method is that measurements are taken whilst no current is flowing in the circuit. This circumvents the possible effect of ohmic impedances which, in the case of dilute solutions, can be appreciably larger than the capacitative impedance and thus impair the precision of the capacity measurements. Measurements have been successfully carried out in solutions as dilute as 10^{-5} N using the commutator method.

The principle of the a. c. method of measuring differential capacity consists in the application of a low-amplitude sinusoidal voltage to the electrode, which is independently polarised to the desired potential from a direct-current source. When the electrode is ideally polarisable the following equation gives to the value of the alternating current flowing (i):

$$i = \frac{\Delta\varphi}{\sqrt{R^2 + \frac{1}{C^2\omega^2}}}, \qquad (3)$$

where $\Delta\varphi$ is the amplitude of the alternating voltage, $\omega = 2\pi\nu$ is the angular frequency, C is the double layer capacity, and R is the resistance of the solution. Eqn. (3) states that the measured current becomes proportional to the double layer capacity if the resistance of the solution is made low enough. This is the basis of Breyer and Hacobian's "tensammetric" method[52,53] of measuring differential capacity, in which the alternating current flowing through a polarographic cell containing a sufficiently concentrated solution of an inactive electrolyte is measured. If the resistive term, due to the solution, is small compared with the reactance of the electrode (*i.e.* if $R \ll 1/C\omega$), it becomes possible to evaluate the double layer capacity simply by comparing the a.c. potentials developed across the experimental cell with that across a standard capacitor, since Eqn. (3) now becomes

$$C_x \simeq C_{st} \frac{\Delta\varphi_{st}}{\Delta\varphi_x}, \qquad (3a)$$

and the ratio $\Delta\varphi_{st}/\Delta\varphi_x$ may be measured with an oscilloscope or an a.c. valve voltmeter. This comparison method has been described in detail by Borisova, Proskurnin, and Vorsina[54,55]. It enabled Proskurnin and Frumkin to carry out the first reliable measurements of double layer capacity[27]. The comparison method, using single-phase current, has been used to measure capacity in solutions[55] as dilute as 10^{-4} N. The resonance method (Watanabe *et al.*[56]) depends on the observation of resonance in a circuit in which the double layer of an ideally polarisable electrode provides the capacitance. It can only be applied if the solutions are sufficiently concentrated, as no resonance can be observed when the ohmic resistance of the solution is too high. Lastly, the impedance bridge method must be included in the a.c. methods of measuring double layer capacity. It provides the most accurate measurements, with ideally polarised electrodes, provided that the total concentration of the electrolyte is not less than millimolar. Essentially, the method consists in keeping two of the arms of an a. c. bridge constant (non-inductive resistances, or capacitances) and matching the double layer capacity and the solution resistance with a variable capacitor and a variable resistor, connected in series. Bridge balance is observed as the disappearance of the potential difference across the bridge. The use of a bridge circuit makes it possible to match the capacitance and the resistance separately, which is particularly advantageous when the phase-lag between current and voltage is appreciably different from 90°. The application of the impedance bridge method to the measurement of differential capacity has been discussed, particularly in papers by Grahame[57-60], Melik-Gaikazyan and Dolin[61,62], Gerischer[63], and Damaskin[64].

The measured capacity of an ideally polarisable electrode will be independent of the frequency of the a.c. employed, provided that the time required for the formation of the double layer is less than one-half of the periodic time. Ferry's[65] and Grahame's[58] calculations showed that the double layer is formed in under 10^{-6} sec in 1 N solutions; the changes in double layer capacity resulting from the use of alternating current and consequent fluctuations in ionic concentration are considerably smaller than the experimental error. An unexplained frequency-dependence of capacity has nonetheless been frequently reported[4,22,23,66-68] ("capacity dispersion"). Grahame[58], Melik-Gaikazyan and Dolin[61,62], and Damaskin[64] have shown that this effect is due to the cell geometry and circuits used, and means for overcoming it have been devised. Thus, the constancy of the differential capacity of a mercury electrode has been demonstrated experimentally over the frequency range 20–500 000 c/s in 1 N KCl solution[61,62] and up to 10 000 c/s in 0.01 N KCL solution[64].

3. VIEWS ON THE STRUCTURE OF THE ELECTRICAL DOUBLE LAYER

Present-day views on the structure of the electrical double layer are based on Stern's theory[69], put forward in 1924. Whilst retaining the basic approach of the earlier theories (Helmholtz[70] and Gouy–Chapman[71,72]), Stern's theory takes into consideration the finite size, the thermal motion, and the specific adsorption of ions. Stern believes that the ionic layer consists of two parts: the fixed, or Helmholtz, part and a diffuse part. The thickness of the fixed part is of atomic dimensions, and the density of the ions which reside in it can be calculated from the Langmuir adsorption isotherm, allowing for specific adsorption forces as well as electrostatic attraction forces. The charge in the diffuse part of the double layer is calculated from Gouy and Chapman's theory. Stern's theory therefore provides the following equation for the surface charge

in the case of a uni-univalent electrolyte:

$$\varepsilon = -\varepsilon_1 - \varepsilon_2 , \tag{4}$$

$$\varepsilon = K_H(\varphi_a - \psi_1) = dF\left[\frac{1}{2+\frac{1}{C}\exp\left(\frac{\Phi_- - \psi_1 F}{RT}\right)} - \frac{1}{2+\frac{1}{C}\exp\left(\frac{\Phi_+ + \psi_1 F}{RT}\right)}\right] + 2\cdot\sqrt{\frac{DRI}{2\pi}}\,c\sinh\left(\frac{\psi_1 F}{2RI}\right), \tag{5}$$

where ϵ_1 is the charge in the fixed layer; ϵ_2 is the charge in the diffuse layer; K_H is the integral capacity of the fixed layer; φ_a is the electrode potential, measured from the point of zero charge, ψ_1 is the potential at a distance $r = d/2$ from the electrode surface (mean ionic radius); Φ_+ and Φ_- are the so-called specific adsorption potentials, assumed independent of the electrode potential; D is the dielectric constant; c is the electrolyte concentration; F is Faraday's constant.

An analysis[69,73-75] of Eqn. (5) shows that Stern's theory is in keeping with numerous experimental findings. Thus, the theory explains why the measured double layer capacity is effectively equal to the capacity of a condenser of molecular dimensions in spite of the fact that most of the charge is distributed over the diffuse layer. It can explain charge reversal of the surface, since the potential ψ_1 is not the same as the electrode potential, and can change its sign under the influence of sufficiently strong specific adsorption of ions of the appropriate sign. Since the ζ-potential in not too concentrated solutions may be equated[75] (to a first approximation) to the ψ_1 potential, Stern's theory can be used in the interpretation of electrokinetic phenomena. Besides predicting the shrinkage of the diffuse layer with increasing the electrolyte concentration, the theory gives the variation of ψ_1 potential with electrolyte concentration and with electrode potential. We can therefore assert that Stern's theory, notwithstanding later refinements, should still be regarded as providing the basic modern interpretation of the structure of the electrical double layer.

1. The double layer in the absence of specific adsorption. A quantitative verification of Stern's theory in the absence of specific adsorption ($\Phi_+ = \Phi_- = 0$) has been presented by Vorsina and Frumkin[76]. Assuming fairly low coverage of the surface by adsorbed ions, it can readily be shown from Eqn. (5) that

$$\varepsilon = K_H(\varphi_a - \psi_1) = 2cdF\sinh\left(\frac{\psi_1 F}{RT}\right) + 4c\lambda F\sinh\left(\frac{\psi_1 F}{2RT}\right), \tag{6}$$

where $\lambda = \sqrt{\frac{DRT}{8\pi cF^2}}$ is the thickness of the ionic atmosphere for a uni-univalent electrolyte. The variation of φ_a, the electrode potential, with ψ_1-potential, may be derived from Eqn. (6):

$$\varphi_a = \psi_1 + \frac{2cd\,F}{K_H}\sinh\left(\frac{\psi_1 F}{RT}\right) + \frac{4c\lambda F}{K_H}\sinh\left(\frac{\psi_1 F}{2RT}\right). \tag{7}$$

However, in contrast with Stern's original assumptions, the fixed layer capacity K_H is not constant but varies with potential. If we assume that the fixed layer capacity depends on the sign of the adsorbed ions and varies with coverage by anions and cations as would two separate condensers connected in parallel, and if we further assume that the population of anions and cations in the fixed layer obeys Boltzmann's distribution law, we can derive the following expression for K_H:

$$K_H = \frac{K_H^- \exp\left(\frac{\psi_1 F}{RT}\right) + K_H^+ \exp\left(-\frac{\psi_1 F}{RT}\right)}{\exp\left(\frac{\psi_1 F}{RT}\right) + \exp\left(-\frac{\psi_1 F}{RT}\right)}, \tag{8}$$

where K_H^+ and K_H^- are the integral capacities of the fixed layer for cations and anions respectively (assumed values $K_H^+ = 20\ \mu F\ cm^{-2}$, $K_H^- = 38\ \mu F\ cm^{-2}$). From Eqns. (6), (7), and (8) we may derive the following expression for the differential capacity of the double layer

$$C = \frac{d\varepsilon}{d\varphi} = \frac{d\varepsilon}{d\psi_1}\frac{1}{\left(\frac{d\varphi}{d\psi_1}\right)} = \frac{K_H A}{A + K_H - \frac{1}{2}(K_H^- - K_H^+)\frac{(\varphi_a - \psi_1)F}{RT}\cosh^{-2}\left(\frac{\psi_1 F}{RT}\right)} \tag{9}$$

where $A = \frac{2cF^2}{RT}\left[d\cosh\left(\frac{\psi_1 F}{RT}\right) + \lambda\cosh\left(\frac{\psi_1 F}{2RT}\right)\right]$.

Vorsina and Frumkin[76] calculated C vs. φ curves from Eqns. (9) and (7) and compared them with differential capacity curves measured in dilute solutions of KCl or HCl. A measure of agreement was found, but the calculated curves lay appreciably below the experimental curves (see Fig. 1). It follows that the double layer in KCl or HCl solution is more densely populated than the theory predicts. Up to a point, the results may be explained by invoking the specific adsorption of chloride ions. However, certain inconsistencies arise in Stern's equation for the case of no specific adsorption ($\Phi_+ = \Phi_- = 0$). Thus, the whole of the charge of the ionic layer which is equal to the charge on the electrode, is now relegated to the diffuse layer, *i.e.* $\epsilon = -\epsilon_2$, whence, from Eqn. (4), $\epsilon_1 = 0$. The same result does not follow from Eqn. (5), and the significance of the fixed layer charge obtained for $\Phi_+ = \Phi_- = 0$ is therefore unclear. Better consistency, in the absence of specific adsorption, is found if the following equation[77] is adopted for the surface charge in a uni-univalent electrolyte:

$$\varepsilon = -\varepsilon_2 = 2\sqrt{\frac{DRT}{2\pi}}\,c\sinh\left(\frac{\psi_1 F}{2RT}\right). \tag{10}$$

This is equivalent to regarding the double layer as two capacitances connected in series: the fixed layer capacitance, C_H, and the diffuse layer capacitance, C_D:

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_D}. \tag{11}$$

The physical significance of Eqn. (11) is easily visualised in terms of two imaginary layers of charge in the fixed layer: one equal in magnitude and opposite in sign to the charge on the electrode surface, the other equal and opposite to the charge in the diffuse layer. Since $\epsilon = -\epsilon_2$, the algebraic sum of these two hypothetical charged layers vanishes in this case, and the series combination of capacitors C_H and C_D has a common, uncharged plate.

Grahame has suggested[77] that in the absence of specific adsorption the fixed layer capacitance depends on the surface charge (ϵ) but not on the electrolyte concentration. If this is the case, a C_H vs. ϵ curve can be constructed by applying Eqn. (11) to differential capacity data obtained at any one concentration, and hence capacity curves for any arbitrary concentration can be derived from the observed values of C_H and the calculated values of C_D. Calculations of this type were carried out by Grahame (Fig. 2) for sodium fluoride solutions (which do not give specific adsorption) in water at different temperatures[78,79] and also in methanol[80]. The satisfactory agreement between calculated and experimental curves is convincing proof of the correctness of the assumption that the fixed layer capacity is independent of

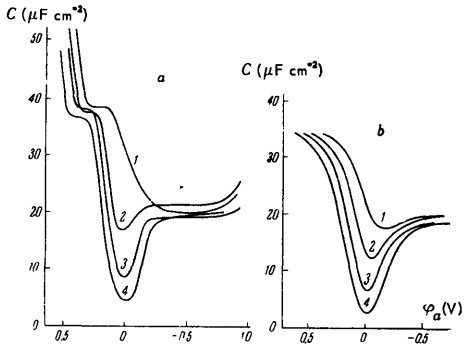


Fig. 1. Variation of differential capacity with electrode potential:
a) experimental curves, measured in the following solutions:
1) 0.1*N* KCl; 2) 0.01*N* KCl; 3) 0.001*N* KCl; 4) 0.0001*N* HCl;
b) calculated from Eqns. (9) and (7) for the same concentrations of a uni-univalent electrolyte.

the concentration of electrolyte when specific adsorption is absent. Furthermore, the classical theory of the diffuse double layer[71,72] is seen to be applicable, in practice, to a greater extent than might have been expected from the numerous simplifying assumptions made.

Actually, several improvements in the diffusion layer theory were suggested shortly after its original publication. Bikerman[81] and Freise[82] calculated the work required to convert dipolar water complexes to dipolar hydrated ion complexes, and were able to allow for the effect of ionic volume on ionic interaction (repulsion effect). Macdonald and Brachman[83] obtained an exact solution of the Debye–Hückel equation, giving the variation of local potential with distance from the polarised electrode, and Macdonald[84] applied this result to the evaluation of the static space-charge in the diffuse layer. Grahame[85] studied the effect of dielectric saturation (decrease in dielectric constant at high electric fields) on the properties of the diffuse layer, and showed that the field strength in the diffuse layer may reach the value 3×10^6 V/cm, above which a rapid drop in dielectric constant ensues. The physically observable properties of the diffuse layer (ψ_1-potential, values of the ionic components, free energy of hydration of ions) are nevertheless relatively unaffected by the onset of dielectric saturation. Sparnaay[86] further refined the theory of the diffuse layer by allowing for the ultimate ionic volume as well as for dielectric saturation. Brodowsky and Strehlow[87] also contributed to this work by showing that both effects act in the same sense and decrease the differential capacity of the diffuse layer. Finally, Kir'yanov and Levich[88], using Bogolyubov's method of correlation functions, derived a coherent statistical theory of the electrical double layer which takes account of the discrete charge distribution in the diffuse layer.

All these refinements of the theory of the diffuse layer introduce serious complications in the mathematical equations, which often cannot be solved analytically. Also, deviations from the classical diffuse layer theory are mostly confined to cases of high surface charge (as shown by Grahame[77]), where the diffusion layer capacity is large compared with that of the fixed layer. It follows, since C_H and C_D are in series connection [see Eqn. (11)], that even relatively large errors in the simple theory will usually lead to negligible errors in the description of the properties of the double layer. This conclusion was strikingly confirmed by Grahame's measurements[78-80] of double layer capacity in sodium fluoride solutions to which we have already referred. At the same time, since the classical theory[71,72] of the diffuse layer was confined to *n*-*n*-valent electrolytes[77], there was a need for extending it to include electrolytes of asymmetrical valency type. Grahame[89] solved the problem for the case of electrolytes of valency types 1 : 2 and 2 : 1.

Macdonald[90,91] attempted to formulate a mathematical theory of the fixed layer in the absence of specific adsorption. In his first paper[90] he gives a mathematical treatment of the concentration-dependence of differential capacity at the point of zero charge. The later paper[91] extends this treatment to arbitrary values of potential, taking account of dielectric saturation in the fixed layer and of the compression of the fixed layer due to strong electric fields. In this case, unlike the case of the diffuse layer, dielectric saturation has a marked effect. Using Grahame's experimental results for sodium fluoride solutions[78], Macdonald obtained a satisfactory measure of agreement between the calculated and the experimental differential capacity curves

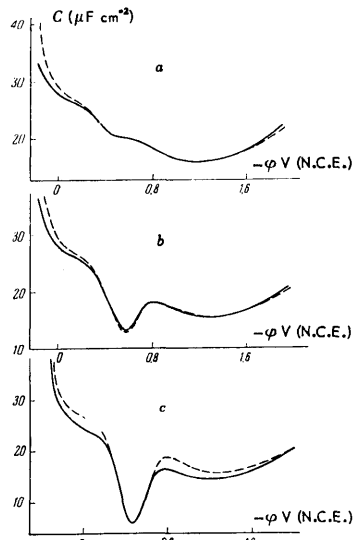


Fig. 2. Differential capacity curves in aqueous NaF solutions at 25°:
a) 0.1*N*; *b*) 0.01*N*; *c*) 0.001*N*; continuous lines: experimental; broken lines: calculated from Eqn. (11) on the basis of experimental results obtained in 0.916*N* NaF.

for a negatively charged mercury surface. As a result of this comparative work he determined a number of the parameters which characterise the properties of the fixed part of the double layer in the absence of specific adsorption. With positively charged surfaces, however, the discrepancies occurred between calculated and measured differential capacities; these were ascribed by the author to the inadequacy of the assumption of no specific adsorption of fluoride anions and that no reliance can be placed on the results.

2. The double layer in the presence of specific adsorption. The early measurements of surface tension[16,19] showed that certain anions have a striking tendency to give specific adsorption at the mercury electrode surface, an observation subsequently confirmed by differential capacity measurements[92,93]. Vorsina and Frumkin, for example, showed[92] that as the adsorbability of the anion was increased (from Cl^- to I^-) the minimum capacity, close to the point of zero charge, increased and became displaced towards more negative potentials. In the presence of I^-, a sharp minimum in the differential capacity curve is observed only if the solutions are as dilute[51] as 10^{-5} N, providing evidence of the strong specific adsorption of this ion. Grahame *et al.*[93] measured differential capacity curves in 12 solutions of potassium salts with different anions, and discussed their results in terms of increasing adsorbability of the anion with decreasing solubility of the corresponding mercurous salt. They concluded that the specific adsorption of anions at a mercury surface is controlled by the covalent forces arising in the crystal lattice of the resulting mercurous salt. Grahame subsequently showed[94,95] that, with the notable exception of the fluoride ion, all singly charged anions exhibit specific adsorption, to a greater or lesser extent, at the mercury electrode surface. It was as a result of this work that Grahame decided, as mentioned above, to use differential capacity curves in sodium fluoride solutions to test the theory of the double layer in the absence of specific adsorption[78-80].

Stern assumed that the specific adsorption of ions was analogous to the adsorption of gases by solid surfaces in obeying Langmuir's adsorption isotherm. The chemical potential of the adsorbed species could then be expressed as

$$\mu_i = \mu_{0i} + RT \ln \frac{\theta_i}{1-\theta}, \qquad (12)$$

where θ is the fraction of the sites occupied by adsorbed particles. For the case of the double layer, Eqn. (12) predicts non-interaction between anion and cation adsorption, which is not acceptable in general. Esin and Markov[96] gave a more accurate expression for ϵ_1 by using a composite Langmuir isotherm for anions and cations, based on the following equations for the chemical potentials of the cations and anions which are adsorbed to different extents:

$$\left.\begin{aligned} \mu_+ &= \mu_{0+} + RT \ln \frac{\theta_+}{1-\theta_+-\theta_-} \\ \mu_- &= \mu_{0-} + RT \ln \frac{\theta_-}{1-\theta_+-\theta_-} \end{aligned}\right\}. \qquad (13)$$

Kambara[97] introduced further refinements of this type into Stern's theory. In deriving the composite Langmuir isotherm Kambara made allowance for the adsorption of surface-active materials and of solvent molecules as well as for the specific adsorption of cations and anions. He obtained an expression for ϵ_1, the charge density, in terms of the ψ_1-potential, and was thus able, after making certain assumptions, to express the charge density at the electrode and the differential capacity as a function of the electrode potential. Unfortunately, all these expressions are extremely cumbersome, and Kambara's theory is therefore difficult to test. Furthermore, Parsons states[98] that the Langmuir isotherms, on which Stern's and Kambara's theories are based, is not really applicable to the specific adsorption of anions, such as I^-, Br^-, CNS^- on a mercury surface. After a detailed study of the adsorption isotherm on mercury of the surface-active iodide ion, Parsons showed[98] that the experimental results were best fitted by Temkin's equation

$$\Phi = \int_{-\infty}^{\mu} \frac{\epsilon_1}{F}\, d\mu = a\, \Gamma_-^0, \qquad (14)$$

or by any other theoretical isotherm leading to Eqn. (14) for appreciable surface coverage. In this respect Langmuir's equation is entirely unsatisfactory and fails to explain the experimental results on the adsorption of I^-, Br^-, CNS^- anions at a mercury surface. There are two reasons for this failure of Langmuir's isotherm: localised adsorption sites are hardly likely to exist at a liquid mercury surface, and furthermore the interactions between charged particles in a discrete distribution of charge, such as exists in the electrical double layer, cannot be ignored.

A further important shortcoming of Stern's, and also of Kambara's, theories is the fact that the locus of the electrical centres of specifically adsorbed ions is identified with the boundary of the diffuse layer. Stern's theory involves only a single potential (ψ_1) at the boundary of the Helmholtz layer. In his study of the experimental results on adsorption at potentials close to the electrocapillarity maximum, Grahame showed[77] that Stern's theory leads to incorrect shifts in the point of zero charge for various anions. To explain the observed shifts which are much larger than predicted by Stern's theory, we must postulate the existence of two distinct Helmholtz layers at different potentials. The locus of the electrical centres of the specifically adsorbed ions is called the inner Helmholtz plane by Grahame, who considers that only anions (with the exception of fluoride[94,95]) can be specifically adsorbed and

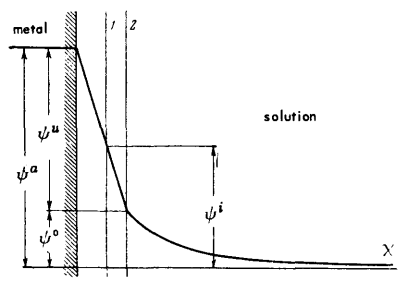


Fig. 3. Structure of the electrical double layer (after Grahame[105]):
1) inner Helmholtz plane; 2) outer Helmholtz plane.

thus give rise to an inner Helmholtz plane. Monatomic cations, which are not specifically adsorbed and are therefore excluded from the inner Helmholtz plane, cannot be part of the fixed layer, and their electrical centres may approach the surface only as far as the outer Helmholtz plane. Grahame stresses[77] that, in contrast with Stern's theory, the outer Helmholtz plane cannot be thought of as an ionic layer but merely represents the position of closest approach to the surface of ions still undergoing thermal motion. Grahame designates the potentials of the inner and the outer Helmholtz planes at ψ^i and ψ^0 respectively (see Fig. 3). Grahame's views on the electrical double layer[77,94], which deny any specific adsorption of cations, allow the charge distribution in the various parts of the double layer and the potential of the outer Helmholtz plane to be calculated, in this particular case, from differential capacity data.

Let us consider Grahame's method of calculation in some detail and confine ourselves, for simplicity, to the case of a uni-univalent electrolyte.

From the thermodynamic theory of the ideally polarisable electrode[77] [see also Eqn. (1)]:

$$F\Gamma_+ = -\int C_+ d\varphi + K_1 , \qquad (15)$$

$$C_+ = \int \left(\frac{dC_+}{d\varphi}\right) d\varphi + K_2 , \qquad (16)$$

$$\frac{dC_+}{d\varphi} = -F\left(\frac{\partial C}{\partial \mu}\right)_{\varphi^-} . \qquad (17)$$

In these equations C_+ is the part of the differential capacity due to the presence of the cation in the double layer; K_1 and K_2 are integration constants; μ is the chemical potential in the solution; the subscript $(\ldots)_{\varphi^-}$ indicates that the derivative refers to a potential measured against that of an electrode reversible to the anion. The right-hand side of Eqn. (17) may be evaluated experimentally from the variation of differential capacity with electrolyte concentration. One can thus find $dC_+/d\varphi$ as a function of the electrode potential φ.

At sufficiently negative potentials, and in the absence of specific adsorption of cations, all the ions will be found in the diffuse layer (*i.e.* $\epsilon = -\epsilon_2$). The kinetic theory of the diffuse layer then gives the following equations:

$$F\Gamma_+ = \epsilon_2^+ = \sqrt{\frac{DRT}{2\pi}c}\,(v + \sqrt{1+v^2} - 1) , \qquad (18)$$

$$C_+ = -\frac{d\epsilon_2^+}{d\varphi} = \frac{C}{2}\left(1 + \frac{v}{\sqrt{1+v^2}}\right) , \qquad (19)$$

where ϵ_2^+ is the charge in the diffuse layer atrributable to the cation, and

$$v = \frac{\epsilon_2}{2\sqrt{\frac{DRT}{2\pi}c}} = -\frac{\varepsilon}{2\sqrt{\frac{DRT}{2\pi}c}} .$$

From Eqns. (18) and (19) we can determine Γ_+ and C_+ uniquely, and thus derive the integration constants K_1 and K_2.* Knowing K_1 and K_2, it is a simple matter to calculate the surface density of the cation Γ_+ from Eqns. (16) and (15), and hence, using the equation

$$(\Gamma_+ - \Gamma_-) F = -\varepsilon \qquad (20)$$

to find the surface density of the anion Γ_-. If no cations are specifically adsorbed at any potential:

$$F\Gamma_+ = \varepsilon_2^+ . \qquad (21)$$

Thus, if we know ϵ_2^+, we can calculate the potential of the outer Helmholtz plane, ψ^0, from the kinetic theory of the diffuse layer:

$$\varepsilon_2^+ = \sqrt{\frac{DRT}{2\pi}c}\cdot\left(e^{-\frac{F\psi^0}{2RT}} - 1\right) . \qquad (22)$$

Finally, it is not difficult to evaluate the anion charge in the fixed layer (ϵ_1) and that in the diffuse layer (ϵ_2^-), since

$$\varepsilon_2^- = -\sqrt{\frac{DRT}{2\pi}c}\left(e^{\frac{F\psi^0}{2RT}} - 1\right) , \qquad (23)$$

$$\varepsilon_1 = -F\Gamma_- - \varepsilon_2^- . \qquad (24)$$

To calculate the potential of the inner Helmholtz plane (ψ^i) further assumptions are required. These will be discussed below.

In Stern's theory the specific adsorption is described in terms of the potentials Φ_+ and Φ_- [see Eqn. (5)], which are assumed to be independent of the electrode potential and therefore also of the surface charge. Grahame's work[77], however, showed that this assumption was contrary to the experimental data. A theory of the electrical double layer in which the influence of the electrode charge on the extent of specific adsorption is duly considered was put forward by Devanathan[99]. It assumes the presence of two Helmholtz planes: an inner plane, the site of the electrical centres of the specifically adsorbed ions which are dehydrated on the side nearest the electrode, and an outer plane (which Devanathan calls the Gouy plane) representing the locus of the electrical centres of the hydrated ions not specifically adsorbed*. Devanathan called the electrostatic capacity of the inner section of the double layer K_{H_1} and that of the section between the two Helmholtz planes K_{H_2}, and by assuming that these capacities are not a function of the electrode charge ϵ, derived the following equation for the overall differential capacity of the double layer

$$\frac{1}{C} = \frac{1}{K_{H_1}} + \left(\frac{1}{K_{H_2}} + \frac{1}{C_D}\right)\left(1 + \frac{d\varepsilon_1}{d\varepsilon}\right) , \qquad (25)$$

where ϵ_1 is the charge due to specifically adsorbed ions and C_D is the double layer capacity, expressed in terms of the charge in the diffuse layer ($-\epsilon - \epsilon_1$) and the electrolyte concentration. For example, in the case of a uni-univalent electrolyte at 25°,

$$C_D = 19.45\sqrt{138c + \varepsilon_2^2} , \qquad (26)$$

where C_D is in $\mu F\ cm^{-2}$, ϵ_2 is in $\mu C\ cm^{-2}$, and c is in M.

Eqn (25) shows that the double layer is equivalent, according to Devanathan's theory, to three condensers connected in series, of capacities K_{H_1}, K_{H_2}, and C_D. The latter two capacities require a correction for the change in

* K_1 and K_2 can also be derived, though less accurately, from electrocapillary curves[94].

* Devanathan identifies the concept of specifically adsorbed ions with that of ions which lose their water of hydration upon being adsorbed, and therefore dissents from the generally adopted view that specific adsorption – like other adsorptions – involves forces other than purely electrostatic ones (*e.g.*, covalent, or van der Waals forces). See also ref. 48.

specific adsorption with surface charge. The same author showed[99] that $d\epsilon_1/d\epsilon$ could be evaluated from experimental data on differential capacity by introducing certain assumptions into Eqn.(25); the charge due to specifically adsorbed ions, ϵ_1, can then be derived by numerical integration. Calculations of the surface densities of the cations and anions (Γ_+ and Γ_-) and of the shift in the point of zero charge produce results in satisfactory agreement with experiments based on this theory. Most of the parameters which appear in Eqn. (25), however, (namely K_{H_1}, K_{H_2}, and $d\epsilon_1/d\epsilon$), have to be experimentally determined. Devanathan's theory of the electrical double layer is thus seen to be essentially semi-empirical. Exception could also be taken to the assumption that the fixed layer capacities K_{H_1} and K_{H_2} are independent of the surface charge. One consequence of this assumption seems particularly difficult to accept, namely that for any electrolyte, specific adsorption can be suppressed only at the minimum of the C *vs.* ϵ curve ($\epsilon \simeq$ $\simeq -13\ \mu C\ cm^{-2}$), *i.e.* that all ions retain their hydration shell at this particular value of the surface charge. Finally, it may be noted that Devanathan's theory, like Stern's, ignores the discrete nature of the specifically adsorbed ionic charge.

Frumkin commented[73] as long ago as 1935 on the undesirability of neglecting the discrete structure of the double layer, as is done in Stern's theory. Discrepancies between this theory and experimental findings were first reported in 1939 by Esin and Markov[96], who observed an anomalously large shift in the point of zero charge as a function of potassium iodide concentration. On the basis of the equation

$$\varphi_{zc}^{(KJ)} - \varphi_{zc}^{(NaF)} = \psi_1 \simeq \text{const.} - \frac{RT}{F} \ln c_{(KI)} \qquad (27)$$

derived from Stern's theory, the zero-charge potential $\varphi_{zc}^{(KI)}$ was expected to vary linearly with $\log c_{(KI)}$, with a slope of not more than 58 mV per factor of ten change in concentration. Esin and Markov found that the relationship was indeed linear, but their experimental slope ($\sim$ 100 mV per factor of ten) exceeded the expected value by a factor of two. Esin and Shikhov explained[100] this result by postulating anion–cation dipoles on the electrode surface, situated in a hexagonal array. The difference in potential between the anion and the cation layers would then be only a fraction of the potential difference due to two separate layers of charge. No fixed anion–cation dipoles can in fact exist in the double layer, and the Esin–Shikhov model therefore leads to an even steeper variation of point of zero charge with the logarithm of KI concentration ($\sim$ 200 mV per factor of ten) than was observed in practice.

A further development of the theory of discrete ionic distribution in the double layer is due to Ershler[101]. This worker abandoned the Esin–Shikhov dipole model and put forward a different, more accurate picture of the charge distribution in the double layer for the particular case of the zero charge potential. By considering the multiple reflection of the charges of the specifically adsorbed anions between two equipotential surfaces (the outer Helmholtz plane and the metal surface) Ershler was able to prove that the potential difference between these two surfaces should be just one-half of that calculated from the Esin–Shikhov anion–cation dipole model. Ershler's theory[101] satisfactorily explained the results of experiments on the dependence of the shift in zero-charge potential upon the concentration of specifically adsorbed anions[96,102]. Gurenkov subsequently showed[103] that Ershler's theory was equally satisfactory when applied to experiments on the concentration-dependence of adsorption potential at the solution/air interface, although it had originally been developed for the metal/solution interface. It should be noted that the principles underlying the calculation of adsorption potentials in concentrated solutions[102,103] were put forward by Frumkin[104].

More recently, Grahame[105,106] has developed Ershler's views and applied them to the case of charged surfaces, and has studied the potential drop in the diffuse layer. According to Grahame[105],

$$\varphi_a = \psi^u + \psi^0 = \psi^V + \psi^{02} + \psi^0, \qquad (28)$$

where φ_a is the electrode potential relative to the point of zero charge in a non-adsorbed electrolyte (*e.g.* NaF); ψ^u is the potential drop in the fixed layer, made up of ψ^V (potential difference due to specifically adsorbed ions) and ψ^{02} (potential difference arising from the electronic charge of the surface, see Fig. 3). Furthermore,

$$\psi^{02} = \int_0^{\varepsilon} \frac{1}{C^{02}} d\varepsilon, \qquad (29)$$

where C^{02} is the differential capacity of the fixed layer at constant specific adsorption of anions, introduced by Grahame:

$$C^{02} = \left(\frac{\partial \varepsilon}{\partial \psi^u}\right)_{\epsilon_1}. \qquad (30)$$

Knowing φ^0, the potential of the outer Helmholtz plane [see Eqn. (22)], the potential drop across the fixed layer, ψ^u, may be found from Eqn. (28), and C^{02} may then be evaluated for any arbitrary surface charge using Eqn. (30). Grahame's calculations[106] showed that C^{02} is practically independent of ϵ_1, and should therefore be the same for all anions, since at $\epsilon_1 = 0$ the value of C^{02} is not affected by the nature of the anion. This result greatly simplifies the subsequent calculations. In practice, once ψ^{02} has been found by numerical integration of Eqn. (29), it is not a difficult matter to derive ψ^V from Eqn. (28), *i.e.* to evaluate the potential drop in the fixed layer arising from the presence of specifically adsorbed anions. According to the Ershler–Grahame theory[101,105], which postulates a hexagonal array of specifically adsorbed ions on the surface and multiple reflections of their charges between the equipotential surfaces of the metal and of the outer Helmholtz plane,

$$\frac{d\psi^V}{d \ln a_{\pm}} = \frac{1}{\dfrac{RT}{F\psi^V} - \dfrac{d\psi^i}{d\psi^V}} \frac{RT}{F} \qquad (31)$$

[ε = const],

where $\alpha_{\pm}$ is the mean activity of the electrolyte. Eqn. (31) yields a value of $d\psi^i/d\psi^V$ and thus finally leads to a calculated value for ψ^i, the potential of the inner Helmholtz plane. It should be noted that an entirely self-consistent mathametical theory, able to take account of the discrete nature of the charges in the fixed layer, has very recently been developed by Kir'yanov and Levich. Their analysis has confirmed the correctness of Eqn. (31), which lacked a really firm basis in Ershler's[101] and in Grahame's[105] earlier derivations.

In the whole of Grahame's work the assumption is made that cations are not specifically adsorbed at a mercury electrode surface over the entire accessible potential range [see Eqn. (21)]. The assumption is not strictly correct, however, since a few inorganic cations can undergo excess adsorption to a moderate extent.

Vorsina and Frumkin[107] were the first to conclude, from differential capacity data, that the La^{3+} and Th^{4+} cations are specifically adsorbed to some extent at a mercury surface.

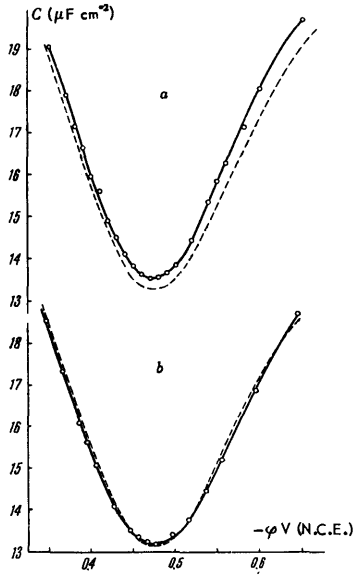


Fig. 4. Portions of differential capacity curves in the neighbourhood of the point of zero charge in 0.01*N* solutions of (*a*) CsF and (*b*) NaF, at 25°. Points and full curves : experimental; dotted curves : calculated from Eqn. (11) on the basis of experimental results obtained in 0.9*N* solutions.

Grahame himself showed[108] that when the mercury surface is negatively charged the double layer capacitance in 0.1 *N* aqueous chloride solutions increases in the sequence $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, but he attributes this effect to changes in the capacity of the fixed layer, arising from the different cation radii and the different dielectric saturation in the fixed layer. The difference in capacity for the cations Li^+, Na^+, and K^+ is even more striking in methanol solutions[109]. The work of Frumkin, Damaskin, and Nikolaeva-Fedorovich[110,111] suggests a ready explanation for the increase in capacity in the series Li^+ to Cs^+ in terms of a relatively small amount of specific adsorption of cations, increasing with ionic radius.

It can be shown, on the other hand, that the difference in differential capacity between solutions of, say, NaF and CsF is not entirely explicable on the grounds of changes in the capacity of the fixed layer. Indeed, it has already been stressed that, in the absence of specific adsorption, the electrical double layer is equivalent to two condensers of capacities C_D and C_H connected in series [see Eqn. (11)], such that the fixed layer capacity C, whilst being a function of the charge on the electrode, is at the same time independent of the electrolyte concentration. Fig. 4 shows portions of differential capacity curves in the neighbourhood of the point of zero charge for 0.01 *N* sodium fluoride and caesium fluoride solutions, as measured by the present author, together with C *vs.* φ curves calculated for the same solutions by substituting data obtained in 0.9 *N* NaF and CsF solutions into Eqn. (11). Clearly, the calculated and the experimental capacity curve coincide only for the sodium fluoride solution, and therefore the assumed absence of specific adsorption of Na^+ and F^- ions is confirmed in this case. With caesium fluoride, on the other hand, the experimental C *vs.* φ curve lies above the calculated curve, and this shows directly that the Cs^+ cation must undergo slight specific adsorption. The presence of some specific adsorption in the case of some inorganic cations is further confirmed by electrocapillarity and zero charge potential measurements[111], and receives indirect support from our extensive knowledge of the kinetics of the electrolytic reduction of numerous ions at the mercury electrode[112].

The effects resulting from the specific adsorption of Cs^+ and La^{3+} are relatively small in comparison with those which accompany the adsorption of anions. There are some inorganic cations, however, such as Tl^+, whose specific adsorbability is entirely comparable with that of the anions Cl^- and Br^-. The adsorption of Tl^+ on mercury causes a sharp drop in the electrocapillary maximum, which is shifted towards more positive potentials[113]. Thallium cations are also strongly adsorbed on a platinum surface[114]. Grahame's theory of the double layer, which postulates that cations are not specifically adsorbed, must therefore be regarded as somewhat approximate.

We should also note that the theory developed by Grahame is not applicable to concentrated electrolytes, when the negative adsorption of ions begins to swamp the electrostatic interaction of these ions with the charged surface. Frumkin and Iofa[115] showed how ion adsorption in concentrated solutions could be evaluated from electrocapillary curves, and Iofa, Ustinskii, and Eiman[116] followed up this suggestion in the case of hydrochloric, hydrobromic, and sulphuric acids. As expected, they found that on the cathodic branch, and for relatively low HCl concentrations, Γ_+ is positive and $(-\Gamma_-)$ is negative. As the acid concentration is increased, in addition to the electrostatic adsorption, general negative ion adsorption begins to be noticeable, and Γ_+ decreases. In really concentrated HCl solutions (> 10 *N*) the adsorption of hydroxonium cations on the negatively charged mercury surface can no longer be calculated from Eqn. (21), basic to Grahame's theory; furthermore, it is actually a negative quantity, since under these conditions the negative adsorption of H_3O^+ ions outweighs their electrostatic attraction. In concentrated sulphuric acid solutions (10.0 – 12.3 *N*) this effect is even more apparent[116].

These specific cation adsorption effects, and the negative adsorption of ions in concentrated solutions, are a searching test for the applicability of Grahame's theory of the electrical double layer. Nevertheless, calculations based on his theory can in many cases lead to important parameters, characteristic of the double layer, which can be used in explaining the kinetics of electrochemical reactions[117].

3. Double layer in the presence of organic surface-active materials. Many organic compounds are adsorbed at the mercury electrode surface. Gouy showed[17,18], as long ago as 1906, that adsorbed organic material can lower the interfacial tension of mercury significantly. His experiments indicated a decrease in the adsorption of neutral organic molecules as the potential drop at the electrode/electrolyte interface was increased, and complete desorption at high enough surface charges. Electrocapillary curves measured in the presence of organic impurities showed breaks of varying degrees of sharpness. The desorption of organic substances at high surface charges arises from the increase in the energy

stored in the double layer capacity when the layer of organic molecules, of low dielectric constant, is replaced by a layer of water molecules whose dielectric constant is significantly higher even allowing for saturation effects[91].

Frumkin developed a quantitative theory[118] of the influence of an electric field on the adsorption of neutral molecules in which the equation of state of the adsorbed layer is considered. Evaluating the attractive forces between adsorbed molecules, he finds the following relationships between the depression of interfacial tension ($\Delta\sigma$), the surface coverage ($\theta = \Gamma/\Gamma_m$), and the concentration of surface-active material (c):

$$\frac{\Delta\sigma}{A} = -\ln(1-\theta) - a\theta^2, \tag{32}$$

$$Bc = \frac{\theta}{1-\theta} e^{-2a\theta}, \tag{33}$$

where A, B, and a are constants such that $A = RT\Gamma_m$, a is a measure of the mutual attraction between adsorbed molecules, and B gives the effect of electrode potential upon the adsorption:

$$B = B_0 \exp\left[-\frac{\frac{1}{2}C_0\varphi_a^2 - \frac{1}{2}C'\varphi_a(\varphi_a - 2\varphi_N)}{RT\Gamma_m}\right], \tag{34}$$

where C_0 and C' denote the capacity of the double layer at $\theta = 0$ and $\theta = 1$ respectively, and φ_N is the shift in point of zero charge when the surface is covered by the adsorbate.

Frumkin's theory[118] satisfactorily explains the measured effects of dissolved surface-active organic substances on the interfacial tension of mercury.

In Butler's theory[119] an attempt is made to explain the observed electrocapillary curves in terms of the molecular properties of the adsorbate (the polarisability of the organic molecules is particularly stressed). However, Butler's theory relies on experimental measurements of interfacial tension to give the dipole moments of the adsorbed molecules. Furthermore, by assuming that Henry's law is applicable, the theory leads to an incorrect relationship between the adsorption of an organic substance and its concentration in solution.

Lippmann's Eqn. (2), applied to electrocapillarity data, predicts for differential capacity curves in the presence of organic additives a region of low capacity ($\sim 4-5\ \mu F\ cm^{-2}$) bounded on both sides by desorption peaks. According to Frumkin[118], the extent of adsorption in fact varies linearly with surface charge. It is, therefore, an easy matter to derive the following equation for the differential capacity:

$$C = C_0(1-\theta) + C'\theta + (\varepsilon' - \varepsilon_0)\frac{d\theta}{d\varepsilon}, \tag{35}$$

where ϵ_0 and ϵ' denote the surface charge at $\theta = 0$ and $\theta = 1$ respectively. The last term in Eqn. (35) is a pseudo-capacity connected with the adsorption–desorption process; this parameter gives rise to peaks in the differential capacity curves. For sufficiently large surface charges, whether positive or negative, $\theta \to 0$, so that one expects from Eqn. (35) that capacity curves measured with and without organic impurities should coalesce in these regions. That such is indeed the case was first demonstrated by Proskurnin and Frumkin[27], who found that differential capacity curves in the presence of n-octyl alcohol were of the expected form. Capacity curves of a similar form were reported by Ksenofontov, Proskurnin, and Gorodetskaya[120] in solutions of ethanol, n-butanol, and phenol. The double layer differential capacity method has since become widely used for studying the adsorption of organic substances at electrode surfaces. For example, it was applied in an investigation[121] of the structure of the thin films formed at the mercury/solution interface by palmitic, oleic, and myristic acids, and by cetyl alcohol. Other recorded uses of the method include studies of the adsorption of valeric acid and other functional derivatives containing five carbon atoms[122] and of the adsorption of various polyelectrolytes, both dissociated and undissociated[123]. Differential capacity measurements enabled Melik-Gaikazyan[124] to demonstrate the formation of multimolecular layers on the surface of a mercury electrode exposed to solutions of n-octanol and n-hexanol. Multimolecular layer formation is accompanied by an even more striking drop in capacity (to as little as $0.9\ \mu F\ cm^{-2}$). Using differential capacity data, Laitinen and Moiser[125] calculated adsorption isotherms on mercury for thirty different organic compounds, and found that the adsorption could be described sufficiently accurately by a Langmuir equation. The adsorption on mercury of the surface-active tetra-alkylammonium cation was studied[126] by the differential capacity method. It was shown that bulky organic cations, such as $[(C_4H_9)_4N]^+$, behave like neutral surface-active molecules on the mercury surface. Thus, in spite of the electrostatic attractive forces, the tetrabutylammonium cation is desorbed from the mercury surface at sufficiently negative potentials, giving a characteristic peak on the differential capacity curve.

More recently, Breiter and Delahay[127] have compared data on the adsorption of n-amyl alcohol on mercury, calculated thermodynamically from electrocapillary curves, with others derived from measurements of double layer differential capacity using Eqn. (35). The good agreement of the two sets of results confirmed the essential correctness of Eqn. (35), which is now commonly used in studies of the adsorption of organic compounds by the differential capacity method.

In a number of cases the differential capacity curve takes an even more complicated form in the presence of organic surface-active molecules and ions. Thus, Loveland and Elving[128] observed four instead of two capacity peaks, due to desorption, in oscillographically displayed differential capacity curves measured in saturated n-heptyl and n-octyl alcohols. They ascribed the two outer peaks to complete desorption of alcohol molecules, and the two inner peaks to the formation (or disappearance) of a second layer of adsorbed molecules which constitutes a micellar film at low electrode charges. Even brief bubbling of an inert gas through the solution is sufficient to decrease the concentration of alcohol in the solution to the point where the differential capacity curve assumes the normal shape with two desorption peaks. Gupta also concluded[129] that condensed, micellar films can be formed, as a result of his "tensammetric" study of the adsorption of methyl orange on mercury. He found entirely similar capacity peaks, due to the formation and the disappearance of micellar films; he also found peaks of this type in the adsorption on mercury of long-chain alkyl sulphonate anions (12 or more carbon atoms)[130,131], and of sodium laurate and caprylate[132].

In the absence of complicating multilayers and micellar films of surface-active organic molecules or ions, differential capacity curves are satisfactorily accounted for by Frumkin's theory[118], at least where the adsorption of saturated aliphatic compounds is concerned. This theory has been extended by American workers[122] and used to

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establish the variation of differential capacity with polarisation and adsorption. Frumkin's theory[118] can also explain the S-shaped adsorption isotherms observed with strongly interacting surface-active molecules[133,134], and with large organic cations[135].

As shown by Gerovich *et al.*[136-138] and also by Blomgren and Bockris[139], the π-electrons present in aromatic and in certain cyclic and aliphatic unsaturated compounds causes these substances to be adsorbed on a positively charged mercury electrode surface. An increase in the positive charge of the surface does not induce desorption: the adsorption of organic molecules containing π-electrons cannot therefore be described as a function of the electrode potential by Frumkin's theory[118]. An attempt was recently made by Parsons[140] to develop a general thermodynamic theory of the structure of the electrical double layer in the presence of adsorbed organic molecules and ions, but no quantitative test could be made as the existing experimental data were inadequate.

Whilst inorganic ions are adsorbed on a mercury surface so rapidly that the time required to form the electrical double layer cannot be measured, even by the most recent methods[61,62], the situation is quite different in the presence of large organic molecules or ions. The kinetics of the adsorption of an organic substance on the mercury electrode surface may be followed by an a.c. method (Frumkin and Melik-Gaikazyan[141,142]). By studying the frequency-dependence of the differential capacity in the neighbourhood of the desorption peaks in solutions containing normal saturated alcohols, Melik-Gaikazyan was able to show, on the basis of Frumkin's theory, that the diffusion of alcohol molecules towards the mercury surface was the slow stage in the adsorption of these alcohols. Frumkin's theory[141] considers only two limiting cases: the rate of the process is determined either by the diffusion of the organic molecule towards the electrode surface or by the adsorption itself. Berzins and Delahay[143], at the cost of introducing some complication into the theory, produced a general solution of the problem, dealing with both the diffusion and the adsorption process at the same time. Their method enables rates of adsorption exchange of up to $\sim 10^{-5}$ mole cm^{-2} sec^{-1} to be measured, corresponding to a time of adsorption (or desorption) of 10^{-4} sec, depending on the high-frequency sensitivity of the impedance bridge used. Lorenz *et al.*[144,145] also contributed to this aspect of the problem. They studied the kinetics of adsorption of a number of organic compounds at the mercury electrode by high-frequency (25–100 kc/sec) differential capacity measurements, and showed that the adsorption time, though measurable, was small. Thus, a rate of adsorption exchange of the order of 10^{-4} mole cm^{-2} sec^{-1} was observed with n-butyl, iso-amyl, and benzyl alcohols, with phenol, methyl ethyl ketone, n-oleic acid, chloroform, and with a number of other organic compounds. Since the maximum extent of adsorption for these substances is (according to Lorenz) about 10^{-9} mole cm^{-2}, the time-constant is in every case $\leq 10^{-5}$ sec. On the other hand, the rate of double condensation which, according to Lorenz[133,134], takes place with organic molecules having sufficiently long carbon chains, is much less than the rate of adsorption. Thus, in the case of the higher fatty acids (C_6, C_8, and C_9) the time-constant for double condensation lies between 10^{-1} and 10^{-3} sec. However, if no double condensation is involved in the overall adsorption process, which includes the diffusion of organic molecules to the electrode surface, the diffusion stage becomes the slowest and determines the rate of the whole process. This is in accordance with Frumkin and Melik-Gaikazyan's conclusions[141,142]. In this connection, Delahay *et al.*[146-148] have made a detailed study of diffusion kinetics in specific systems which is applicable to the transfer of surface-active organic molecules from the bulk of the solution to the electrode surface during the establishment of adsorption equilibrium. Working on the linear portion of the Langmuir adsorption isotherm, *i.e.* near the origin, these authors concluded[146,147] that when the adsorbate is present at low concentrations a considerable time, of the order of minutes, elapses before adsorption equilibrium is established. One must therefore use a stationary rather than a dropping mercury electrode when studying the adsorption of organic substances. If the complete adsorption isotherm of Langmuir is considered (and this can only be done numerically, using a calculator) the time required for the attainment of adsorption equilibrium is found to be somewhat shorter[148], but nevertheless longer than the drop period of the conventional polarographs (3–5 sec). Frumkin and Damaskin's investigation[135] of the effect of the concentration of the $[(C_4H_9)_4N]^+$ cation on surface coverage, using the dropping mercury electrode, demonstrated that in the maximum adsorption region the number of adsorbed ions is determined almost exclusively by ionic diffusion to the mercury surface. This is in agreement with the conclusions of Delahay *et al.*[146-148].

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THE DISSOLUTION OF METALS IN FUSED HALIDES

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I. INTRODUCTION

The dissolution of metals in fused salts is of exceptional importance for many electrometallurgical and thermal processes, such as the production of titanium, magnesium, aluminium, sodium, etc. The ability of metals to dissolve in a fused electrolyte is the most important cause of decrease in current efficiency and deterioration of performance in electrolysis. Moreover, the kinetics of metal thermite processes, such as the magnesium thermite preparation of titanium, also appear to be related to interaction of the metals in the salt phase. Finally, in recent years a successful start has been made in the application of a method of refining metals, based on the reaction of the latter with a fused salt. There are reports of the use of this method for the purification of nickel, and a similar method for refining aluminium has already found general acceptance. All this indicates the considerable practical importance of the question of metal dissolution.

The theoretical side of the question is of no less importance, however. The study of solutions of metals in fused salts yields important information on the nature of reaction in ionic media and on characteristic features of the liquid state. Solutions of metals provide a clear illustration of Mendeleev's well-known hypothesis regarding the chemical nature of solutions.

The dissolution of metals in fused salts was discovered in 1807 by Davy[1,2], who established that during the electrolysis of fused KOH, or when metallic potassium is fused