

Physico-chemical Studies on Surface Active Agents. (IV)

Some Considerations on the Structure of the Electrical Double Layer in the Presence of Surface Active Agents

Akira WATANABE*

(Tachi Laboratory)

Received March 15, 1960

In order to give the fundamental background for the coagulation studies of the preceding papers, the double layer models, in the presence of surface active agents at various concentrations, have been discussed. In the first part, where a review of the recent theories of inorganic double layers were given, some critical accounts were made on the thermodynamic basis of the Stern theory, by considering its relation to the modern theory of electrolyte solutions. It was also shown that the chemical free energy of adsorption was a measurable quantity in an electrochemical system. The second part deals with the various double layer models proposed, the thermodynamic basis of which was given by using the concept of ideal polarised and non-polarisable electrodes. The relation between the zero point of charge and the adsorption parameters was also studied. It was found that the relation between the surface potential and pAg for AgI sols given by Verwey and Kruyt was valid only for a special case where no specific adsorption was taking place.

I. INTRODUCTION

It is clear from the descriptions in Parts 1¹⁾, 2²⁾, and 3³⁾ that all the phenomena are intimately connected with the changes which take place in the electrical double layer of the sol particles due to the adsorption of the surface active agents. Moreover we have so far obtained from coagulation and zeta potential measurements various experimental facts which appear to give important information about this problem. It would, therefore, seem appropriate to summarize them here and to discuss theoretically the manner in which the double layer surrounding a hydrophobic sol particle is modified by the incorporation of a surface active agent into its structure.

Before discussing this problem, it seems helpful for further understanding of the proposed theory of the double layer of surface active agents to give some short accounts on the theories of simple inorganic double layers proposed by various authors, and to clarify the thermodynamic foundations of these theories by relating them to the recent theory of electrolyte solutions.

II. THEORIES OF THE ELECTRICAL DOUBLE LAYER

1. Theory of the Diffuse Double Layer

It is a well known fact that the condenser model of the electrical double layer

* 渡 辺 昌

proposed by Helmholtz⁴⁾ is too simple and, moreover, is contrary to the second law of thermodynamics. This difficulty has been removed in the idea of the diffuse double layer proposed by Gouy⁵⁾ and Chapman⁶⁾.

(i) Fundamental Equations

This theory is based on two fundamental equations, the first being the Boltzmann distribution equation for an ionic species in the solution phase, *viz.*

$$n_i = n_{ib} \exp(-w_i/kT) \quad (1)$$

where n_i is the concentration of the ionic species i , in numbers per cm^3 , at the point in question in the diffuse double layer, n_{ib} its bulk concentration and w_i the work necessary to bring the ion to this position from a point in the bulk phase where the potential is zero.

In the Debye-Hückel theory of strong electrolytes⁷⁾, which is based on the same principle as the theory of the diffuse double layer, w_i is taken as

$$w_i = z_i e \psi \quad (2)$$

where z_i is the valency of the ionic species of the i -th kind, sign of the charge included, ψ the electrostatic⁸⁾, or cavity⁹⁾, potential at the point in question and e the fundamental charge of an electron. This is, however, not an accurate assumption for the real situation, because it corresponds to taking the ions in the double layer as point charges without any chemical interactions with their environment^{8,9)}. However, it is quite a reasonable assumption as a first approximation, and leads to a satisfactory explanation of the experimental data, as far as the diffuse part of the double layer is concerned.

The second fundamental equation is the Poisson equation, *viz.*

$$\nabla^2 \psi = -(4\pi/\epsilon)\rho \quad (3)$$

where ρ is the volume charge density at the point in question and ϵ the dielectric constant of the medium. Although this equation holds rigorously in any situation, *i. e.* it is a fundamental equation of electrostatics, we must take into account the fact that ϵ is also a function of ψ for high field strengths in the double layer (dielectric saturation)¹⁰⁾. Hence, in a strict sense, the dielectric *coefficient*, dD/dE (where D and E are the dielectric displacement and the field strength, respectively), must be used in equation (3), and not the dielectric *constant*, ϵ . The influence of the dielectric saturation on the theory of the diffuse double layer has been discussed by Grahame¹¹⁾, Booth¹²⁾ and Conway *et al.*¹³⁾, who came to the conclusion that such quantities as the charge of the double layer *etc.* were not altered very much, whereas the potential itself was largely effected by the decrease in ϵ .

On combining equations (1), (2) and (3), we obtain the fundamental equation of the diffuse double layer, namely

$$\nabla^2 \psi = -(4\pi/\epsilon) \sum_i z_i e n_{ib} \exp(-z_i e \psi/kT) \quad (4)$$

The complete solution of equation (4) can be obtained in a simple form only in the one-dimensional case for symmetrical electrolytes¹⁴⁾, where

$$\nabla^2 = d^2/dx^2, \quad z_+ = -z_- = v \quad \text{and} \quad n_{+b} = n_{-b} = n_b.$$

Here, x is the coordinate of the point in question measured from the surface. Since the system as a whole must satisfy the condition of electroneutrality, the surface charge density at the x -plane, σ , is equal to the total charge contained in a column of solution of unit cross section extending from $x=x$ to $x=\infty$ with the sign reversed, *i.e.*

$$\sigma = - \int_x^{\infty} \rho dx.$$

Applying the Gauß law of electrostatics, *viz.*

$$\sigma = -(\varepsilon/4\pi)(d\psi/dx)$$

to the equation of $d\psi/dx$, obtained by integration of equation (4), we obtain

$$\sigma = (\varepsilon k T n_0/8\pi)^{1/2} \sinh (v e \psi/2 kT) \quad (5)$$

Therefore, the differential capacity C is given by

$$C = -(d\sigma/d\psi) = (v^2 \varepsilon e^2 n_0/32\pi kT)^{1/2} \cosh (v e \psi/2 kT) \quad (6)$$

and the potential ψ related to x by^{14, 15)},

$$\psi = \left(\frac{2 kT}{v e} \right) \ln \left[\frac{1 + \gamma \exp (-\kappa x)}{1 - \gamma \exp (-\kappa x)} \right] \quad (7)$$

where

$$\gamma = \frac{\exp (v e \psi_0/kT) - 1}{\exp (v e \psi_0/kT) + 1}$$

and

$$\kappa = (8\pi e^2 v^2 n_0/\varepsilon kT)^{1/2} \quad (8)$$

Here ψ_0 is a constant of integration, *i.e.* $\psi = \psi_0$ for $x = x_0$, which will be discussed later.

Equation (7) can be simplified in the case of the Debye-Hückel approximation, when for $v e \psi_0/kT \ll 1$ or $\psi_0 \ll 25/v$ mV, we obtain

$$\psi = \psi_0 \exp (-\kappa x) \quad (9)$$

and for an arbitrary ψ_0 value, for $\kappa x \gg 1$

$$\psi \cong 4\gamma \exp (-\kappa x) \quad (10)$$

In the case of spherical symmetry, which corresponds to the Debye-Hückel theory of strong electrolytes, we must expand the exponential function and neglect all but the first order term in ψ , in order to obtain a simple form of solution. The relation between the charge density σ , potential ψ and the radial coordinate r is given by

$$\sigma = \frac{\varepsilon \psi_0 (1 + \kappa r)}{4\pi r} \exp [\kappa(r_0 - r)] \quad (11)$$

and

$$\psi = \psi_0 (r_0/r) \exp [\kappa(r_0 - r)] \quad (12)$$

where ψ_0 is the constant of integration, *i.e.* $\psi = \psi_0$ for $r = r_0$.

It is clear from these treatments that κ has the dimension of reciprocal length and is the distance from the plane where the diffuse double layer starts to that

position where the potential drops to $1/e$ of the initial value (e is the base of the natural logarithm).

In the general case of an asymmetric electrolyte, if we assume the first order Debye-Hückel approximation, equation (4) reads

$$\nabla^2 \phi = (4 \pi e^2 / \epsilon kT) \sum_i z_i^2 n_{ib} \phi = \kappa^2 \phi \quad (13)$$

with

$$\kappa = [(4 \pi e^2 / \epsilon kT) \sum_i z_i^2 n_{ib}]^{1/2} \propto I \quad (14)$$

$$\text{and} \quad I = (1/2) \sum_i z_i^2 c_{ib} \quad (15)$$

where c_{ib} is the molality of the i -th ion, I the ionic strength of the solution which defines the double layer thickness, if ϵ and T remain constant, *vide* Part 3⁹. The more accurate calculation of κ in the case of the flat double layer has been worked out by Grahame¹⁰.

(ii) The ϕ_δ -Plane

Although the equations (5) to (12) hold at any point in the diffuse double layer, the most important equations are obtained by taking $x = x_\delta$ or $r = r_\delta$, *i. e.* the position where this layer starts. If we denote the quantities at this plane by the subscript δ , we obtain

$$\sigma_\delta = (\epsilon kT n_b / 8 \pi)^{1/2} \sinh (v e \phi_\delta / 2 kT) \quad (16)$$

$$C_\delta = (v^2 e^2 n_b / 32 \pi kT)^{1/2} \cosh (v e \phi_\delta / 2 kT) \quad (17)$$

or

$$\sigma_\delta = \epsilon \phi_\delta (1 + \kappa r_\delta) / (4 \pi r_\delta) \quad (18)$$

Equation (18) has already been used in Part 2 to calculate the surface charge density from the Stern potential.

(iii) Conclusion

It has been proved by experiments that the theory of the diffuse double layer holds, within the limitations mentioned, for the case of the mercury electrode, and interesting modifications of this theory have been derived in connexion with p- and n-type charge layers in semiconductor materials¹⁷. We can, therefore, consider that the theory of the diffuse double layer is a well established one.

For the case of spherical symmetry, it has been proved by Kirkwood^{18,19}, that only the first order Debye-Hückel approximation fulfills the self-consistency of the system; that is, in the expansion of $\exp \lambda$ it is meaningless to take terms of orders higher than λ^2 .

2. Stern-Grahame Theory of the Double Layer

In discussing the theory of the diffuse double layer in connexion with experiments on the mercury electrode, Gouy and Chapman have used $x_\delta = 0$ or $r_\delta = a$ in equations (16) and (17) or (18) as the boundary conditions, where a is the

particle radius. However, even if $\phi_s=0$, the value of C_s is as high as *ca.* $200\mu\text{F}/\text{cm}^2$ for 1 *M* uni-univalent electrolyte solutions. We must, therefore, introduce another capacity in series to that of the diffuse double layer, in order to obtain the experimental value of *ca.* $30\sim 50\mu\text{F}/\text{cm}^2$ at the zero point of charge. This situation led Stern²⁰⁾ to introduce the concept of an inner adsorption layer which is now called the Stern layer.

It is clear, from the fact that very marked specificity of the anionic species occurs in the anodic polarisation region of the mercury electrode as well as in the range of the zero point of charge, that the anions in the Stern layer must be dehydrated and in direct interaction, by chemical short-range forces, with the mercury surface⁹⁾. On the other hand, as diffuse double layer theory is based on long-range Coulombic interaction operating throughout the dielectricum of water, ionic specificity does not come into any equations. Hence, it is quite natural to consider that it starts from the locus of hydrated ions nearest to the physical surface. Although Stern did not distinguish them, it is very important to stress this point and hence we may denote, following Grahame⁹⁾, the locus of the dehydrated ions as the "inner Helmholtz plane," with subscript 1, and that of the hydrated ions nearest to the surface as the "outer Helmholtz plane," with subscript 2.

In the case of a surface in contact with a simple inorganic salt solution, we can take

$$x_s = x_2, \phi_s = \phi_2, C_s = C_2 \text{ and } \sigma_s = \sigma_2 \quad (19)$$

The theory of the Stern layer is derived by applying the Langmuir equation of adsorption²¹⁾ in the form,

$$n_{i1} = \frac{N_i}{1 + (1/x_{ib}) \exp(\Delta\bar{G}_i/kT)} \quad (20)$$

where n_{i1} is the number of the i -th ions adsorbed per cm^2 in the Stern layer and N_i is the maximum number of available sites, $\Delta\bar{G}_i$ the electrochemical free energy of adsorption and x_{ib} the mole fraction of this ion in the bulk.

Thus $\Delta\bar{G}_i$ can be expressed formally as the sum of the electrical and chemical terms, *i. e.*

$$\Delta\bar{G}_i = z_i e \phi_1 + \Delta G_i \quad (21)$$

Hence,

$$\sigma_1 = \sum_i \frac{z_i e N_i}{1 + (1/x_{ib}) \exp[(z_i e \phi_1 + \Delta G_i)/kT]} \quad (22)$$

If the anionic adsorption is predominant, as is very often the case because of the ease of dehydration of anions compared with that of cations,⁹⁾ we have, for symmetrical electrolytes $z_+ = -z_- = v$

$$\sigma_1 = -v e N_- (1/x_b) \exp[(v e \phi_1 - \Delta G_-)/kT] \quad (23)$$

3. General Consideration of the Theory of the Double Layer

(i) Relation to the Modern Theory of Electrolyte Solutions

In the theory of the diffuse double layer, we have neglected all the chemical work included in w_i of equation (2). However, this is not correct for the case of

concentrated solutions. The concentration in the Stern layer is supposed to be very high compared with the diffuse double layer, even if the Debye-Hückel approximation applies to the latter, and hence equation (4) is not sufficient to explain the whole situation of the double layer.

It is clear from the appearance of equation (20) that the Stern theory is based on some kind of volume exclusion factor, leading to the Fermi-Dirac type of statistics. This is shown by writing the fundamental equation for the conservation of energy of the layer as

$$kT d \ln n_i + z_i e d \phi - V_i n_i z_i e d \phi + d \Delta G_i = 0 \quad (24)$$

where V_i is the volume of the ion. The first term is the osmotic work, the second the electrostatic work, the third the work required to bring the electric charge, of the same volume as the ion, out of the layer to the bulk phase and the last term all the remaining chemical work. By integrating and inserting the constant of integration, we obtain an equation, which is formally similar to the Stern equation (20), *i. e.*

$$\frac{n_{i1}}{n_{ib}} \frac{N_{ib}}{N_i - n_{i1}} = \exp[(z_i e \phi_1 + \Delta G_i)/kT],$$

where $N_{ib} = 1/V_i$ is the maximum number of available sites in the bulk. On the other hand, the Boltzmann distribution, equation (1), is obtained by neglecting all the other terms except the first two in equation (24); this holds in the case of dilute solutions where there is little interaction of the ions with each other and of ions with solvent, *i. e.* ions can be considered as point charges.

The importance of the term containing the ionic volume in equation (24) for the case of concentrated electrolyte solutions has already been clarified by Wicke and Eigen^{22,23}. These authors have been able to explain the various important features of strong electrolyte solutions, *e. g.* the increase in activity coefficient at high concentrations, which could not be explained by the extension of the Debye-Hückel theory. Freise²⁴ has applied this to the diffuse double layer theory. However, it seems that this modification is not important, because the diffuse double layer plays a major part in the whole double layer only in the case of dilute solutions. Moreover, in applying this theory he has neglected the chemical term ΔG_i , and thus the original Stern theory is more complete.

However, it is very useful to apply the Wicke-Eigen theory to explain the properties of sols related to their particle distribution, *e. g.* viscosity, activity *etc.*, because the volume of the sol particles is very much larger than the simple ions; hence the volume effect may become important at more dilute sol concentration than in the case of ionic solutions²⁵.

(ii) Chemical Free Energy of Adsorption

It can be seen from equation (24) that the Stern theory is in principle based on the assumption

$$\begin{aligned} w_i &= \Delta \bar{G}_i - V_i n_{i1} z_i e \phi \\ &= v_i e \phi - V_i n_{i1} z_i e \phi + \Delta G_i \end{aligned} \quad (25)$$

Although Stern has not given details about the last term, it must be remembered

that this is also a function of ψ , The results obtained from experiments with mercury electrodes show that the functional relationship between them is not simple. In this connexion Guggenheim²⁶⁾ has stressed the thermodynamic impossibility of dividing the electrochemical potential $\Delta\bar{G}_i$ into electrical ($z_i e \psi$) and chemical (ΔG_i) terms. Hence, strictly speaking, equation (24) can not be integrated unless the functional relationship between ΔG_i and ψ is known. In the Stern equation ΔG_i was taken as constant and in a certain term an assumption was made such that $1 \gg V_i n_i$.

Various factors can be considered for ΔG_i from a molecular point of view. These are for instance, (a) the work required to displace the polar solvent molecules from the electric field in the double layer²⁷⁾, (b) the work required to push the surrounding ions together to the point, (c) the work required to deform or displace the solvent sheath of the ion when it approaches the surface, *etc.*⁹⁾. Some of these factors have been calculated theoretically by Bolt²⁸⁾ and the factor (c) gives the basis of the Grahame theory of the double layer. Most anions are easily dehydrated on adsorption at surfaces, while most single alkaline cations are difficult to dehydrate and cannot approach nearer to the surface than the outer Helmholtz plane. This factor of dehydration is closely related to the ionic radius; the deformability of the ion is not only related to the ionic radius but also to the field strength at the point²⁹⁾.

Another factor, which is also very important in ΔG_i , is the bond strength between the ion and the surface. This factor must be closely related to the solubility of the salt which is composed of the ionic species to be adsorbed, *e. g.* surface active agent, and the corresponding oppositely charged ions in the surface, *e. g.* silver ions. It is also influenced by the potential at the point of adsorption⁹⁾.

III. THE ELECTRICAL DOUBLE LAYER IN THE PRESENCE OF ADSORBED SURFACE ACTIVE AGENTS

1. Single Layer Adsorption

When a small amount of anionic surface active agent is added to a positive silver iodide sol, the anion appears to be adsorbed on the surface with its negative head group directed to the surface; this is of course partly due to the high surface activity caused by the long chain. As the head group itself, *e. g.* sulphonate *etc.*, has specific adsorbability, it is very likely to dehydrate and make a kind of chemical bond with the silver ion on the surface. It would appear likely, therefore, that the head groups of the surface active agents enter the inner Helmholtz plane together with the other counter ions, say nitrate ions. Hence, the picture of the double layer in this case is not so different from the double layer of simple ions, the outer Helmholtz plane being at the same distance from the surface for both cases, *vide* Fig. 1, (A) and (B). We can put, therefore, the same subscript for the ψ_s -plane as in equations (19), *i. e.*

$$x_s = x_2, \quad \psi_s = \psi_2, \quad C_s = C_2 \quad \text{and} \quad \sigma_s = \sigma_2 \quad (26)$$

However, owing to the different sizes of the head groups and the counter ion, the inner Helmholtz plane will be two-fold, *i. e.*

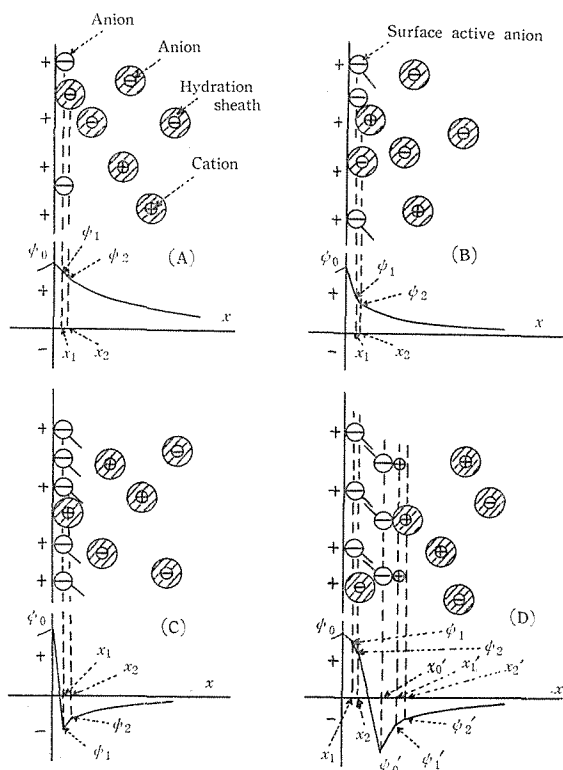


Fig 1. Schematic diagrams of the electrical double layer and potential behaviour.

- (A) Without surface active agent.
- (B) Low concn. of surface active agent.
- (C) Medium concn. of surface active agent.
- (D) High concn. of surface active agent.

$$x_1, x_1^\#; \psi_1, \psi_1^\#; C_1, C_1^\#; \sigma_1, \sigma_1^\#$$

for the head group and counter ion, respectively. For the sake of simplicity, it is assumed in Fig. 1 (B) that these two planes coincide.

At this stage of adsorption the population of the surface active anions on the surface will probably be fairly small. Moreover, the long chain is most likely to lie parallel to the surface rather than have a vertical orientation, *vide* Part 2. Therefore, the structure of the diffuse double layer is not so much influenced by the long chain, although the potential ψ_2 is decreased very much due to the adsorption in the inner Helmholtz plane. On the other hand, it is to be expected that the displacement of the water molecules from the inner Helmholtz plane by the hydrophobic alkyl chains will alter the structure of this layer, for instance by decreasing the dielectric constant, increasing the fluidity, *etc.*

2. Second Layer Adsorption

As the surface active ion concentration is increased, the adsorption of ion will increase, the fundamental relationship being the same as equation (20). However,

the adsorption does not always take place on the first layer only; a second type of adsorption starts to take place at a certain stage, *vide* Part 2. The latter will be propagated by van der Waals attraction between the alkyl chains of the surface active agents. Whether further adsorption of the surface active agents takes place on the first layer, Fig. 1 (C), or on the second layer, Fig. 1 (D), depends on the relative magnitudes of the electrochemical free energies of adsorption, $\Delta\bar{G}_1$ and $\Delta\bar{G}_1'$, as well as on the maximum numbers of available sites, N_1 and N_1' , of these two layers. It must be remembered that N_1' is a function of the degree of coverage in the first layer, and also that $\Delta\bar{G}_1'$ is strongly influenced by the potential ψ_1 .

It is concluded from Fig. 1 (D) that in this case the double layer consists of six layers, *viz.* two ψ_0 -planes, two ψ_1 -planes and two ψ_2 -planes. At this stage the chemical free energy of adsorption on the second layer, $\Delta\bar{G}_1'$, is mainly dependent on the binding energy of the counter ion to the head groups, and hence, the surface has practically the properties of the head group itself rather than the original surface, *i. e.* ψ_0 -plane, see Part 3.

Although we have drawn the ψ_2 - and ψ_2' -planes apart in Fig. 1 (D) to make the difference clearer, the actual situation is more likely that the chain will lay itself parallel to the surface and hence the two planes will not be so different geometrically. Therefore, the potential at this plane has essentially the value of ψ_2' instead of ψ_2 , and we can write

$$x_\delta = x_2', \quad \psi_\delta = \psi_2', \quad C_\delta = C_2' \quad \text{and} \quad \sigma_\delta = \sigma_2' \quad (27)$$

In other words, the diffuse double layer starts from the ψ_2' -plane.

It is interesting in this connexion to discuss the potential behaviour in the double layer, *vide* Fig. 1. It has been proved from Gauß' theorem of electrostatics in Part 1 that the potential distribution in the diffuse double layer is defined only by ψ_δ , and that if ζ equals zero then ψ_δ must also equal zero, even if the plane of shear, where the ζ potential is measured, is somewhere inside the diffuse double layer.

This conclusion sounds contradictory to Guggenheim's statement²⁰⁾ that the absolute potential is not a measurable quantity in the thermodynamic sense. However, as the ζ potential measurement is based on an irreversible process in nature^{30,31)}, it is not unreasonable to suggest that it could be measured. In fact Defay and Mazur³²⁾ have pointed out the possibility of dividing the electrochemical free energy of ions in solution into electrical and chemical terms, which is equivalent to the possibility of absolute potential measurement, on the basis of thermodynamics of irreversible processes.

If the above discussion is correct, the chemical free energy of adsorption on the ψ_1' -plane, $\Delta\bar{G}_1'$, that is the binding energy on a surface covered by surface active agents, has a physical meaning, at least at $\zeta=0$. However, this situation seems unapproachable in practice, because the ψ_2' -plane has usually a high electrical potential.

3. The Application of the Concept of Ideal Non-polarisable and Ideal Polarised Electrodes to Solid Surfaces

The difference between the ideal non-polarisable and the ideal polarised electrodes was clearly defined by Grahame⁹⁾ for the case of a metal surface in contact with

salt solutions. Although both electrodes are in equilibrium in a thermodynamic sense, this difference is of great importance because it gives a completely different picture of the double layer structure.

Basically, the ideal non-polarisable electrode is one whose potential difference is defined by the concentration of an ionic species, *i. e.*

$$\phi = \phi_s + (kT/ze) \ln c_{ib} \quad (28)$$

where ϕ is the Galvani potential difference between the two phases, c_{ib} the concentration (or more rigorously the activity) of the ionic species in question, and ϕ_s the value of ϕ when $c_{ib}=1$ (*i. e.* the standard electrode potential). This means that the ion can freely pass through the interface between the metal and solution. This ionic species, which contributes to the reversible establishment of the electrode potential, is called the "potential determining ion", for instance a silver ion for a silver electrode.

On the other hand, the ideal polarised electrode is one which behaves as if it has a barrier inhibiting the passage of any ionic species through the interface. This description sounds a little indirect, but has been used because it has been proved by Grahame and Whitney³³⁾ that this kind of electrode could exist in equilibrium in a thermodynamic sense. The potential, and hence the surface charge density, of this kind of electrode is defined by the electromotive force applied from an external circuit. Therefore, the concept of the "potential determining ion" loses its meaning here, and the electrical double layer in the solution phase is composed of the ions of the indifferent electrolyte and the dipole molecules only.

It is clear from the above description that the latter system has an extra degree of freedom, because we can change the electrode potential, or the surface charge density, at constant concentrations of the ionic species, including the one in common with the metallic phase (*e. g.* mercurous ion for a mercury electrode). In the case of the former system any slight change in the electrode potential caused by an external electromotive force will disturb the equilibrium of the system and cause a finite current to go through the interface continuously. Here we have neglected the establishment of concentration polarisation for the latter system and the unavoidable small leakage current for the former; for these reasons the adjective "ideal" has been used for both systems.

(i) Application to the Silver Iodide Surface

Let us consider a silver iodide surface in contact with a solution containing silver ions. It is a well known fact that we can make a reversible electrode of this system, which means that the Galvani potential difference between the two phases is given by

$$\phi = \phi_s^{\text{AgI}} + (kT/e) \ln c_{\text{Ag}^+} \quad (29)$$

That is, the potential of the silver iodide, and hence its surface charge density, is completely defined by the concentration of the potential determining ion, *i. e.* silver ion. Therefore, this system gives a typical example of the extension of the ideal non-polarisable electrode to a solid surface, *vide* Discussion in Part 2.

The Galvani potential difference³⁴⁾ is related to the electrostatic potential at the

surface ϕ_0 and the $\Delta\chi$ potential, which will be discussed later, by the following equation³⁵⁾,

$$\phi = \phi_0 + \Delta\chi \quad (30)$$

Substitution of this equation (29) in equation gives

$$\phi_0 + \Delta\chi = \phi_s^{\text{Ag}^+} + (kT/e) \ln c_{\text{Ag}^+} \quad (31)$$

At the zero point of charge, $c_{\text{Ag}^+} = c_{\text{Ag}^+}^0$ and $\phi_0 = \phi_0^0$, when equation (31) becomes

$$\phi_0^0 + \Delta\chi = \phi_s^{\text{Ag}^+} + (kT/e) \ln c_{\text{Ag}^+}^0 \quad (32)$$

The superscript 0 is used to denote the zero point of charge. From equations (31) and (32), we obtain

$$\phi_0 - \phi_0^0 = (kT/e) \ln (c_{\text{Ag}^+} / c_{\text{Ag}^+}^0) \quad (33)$$

This is the equation giving the relation between the surface potential ϕ_0 and $p\text{Ag}$.

The potential of the ϕ_0 -plane at the zero point of charge, ϕ_0^0 , is not always zero, although by definition $\sigma_0^0 = 0$; this does not correspond to $\psi_0^0 = 0$ either. Because of the electroneutrality of the system, the following relation holds;

$$\sigma_1^0 + \sigma_2^0 = \sigma_0^0 = 0,$$

hence

$$\sigma_1^0 = -\sigma_2^0.$$

This means that, at the zero point of charge, the total charge, in the diffuse double layer has the same value as that in the Stern layer with the sign reversed. Here, for simplicity, the case of a clean surface without the coverage of surface active agents is discussed. As is clear from equations (16) and (22), this condition reads

$$\begin{aligned} & (\varepsilon k T n_b / 8 \pi)^{1/2} \sinh (v e \psi_0^0 / 2 k T) \\ &= \frac{v e N_+}{1 + (1/x_b) \exp [(v e \psi_1^0 + \Delta G_+) / k T]} \\ & - \frac{v e N_-}{1 + (1/x_b) \exp [(-v e \psi_1^0 + \Delta G_-) / k T]} \end{aligned}$$

In the case of the Debye-Hückel approximation, this reads

$$\begin{aligned} & (\varepsilon k T n_b / 8 \pi)^{1/2} (v e \psi_0^0 / 2 k T) \\ &= v e x_b [(N_+ - N_-) - (N_+ + N_-) (v e \psi_1^0 / k T) \\ & + (N_- \Delta G_- - N_+ \Delta G_+) / k T] \end{aligned} \quad (34)$$

Hence, when $N_+ = N_-$ and $\Delta G_+ = \Delta G_-$ then $\psi_0^0 = \psi_1^0 = 0$ for the zero point of charge; the most extreme case is $\Delta G_+ = \Delta G_- = 0$, i. e. no specific adsorption in the Stern layer. In this case the following equations hold:

$$\psi_0^0 = \psi_1^0 = \psi_2^0 = \zeta = 0 \quad (35)$$

and

$$\phi_0 = (kT/e) \ln (c_{\text{Ag}^+} / c_{\text{Ag}^+}^0) \quad (36)$$

for an arbitrary concentration of the silver ion, including the zero point of charge. Equation (36) is the same as the one derived by Verwey and Kruyt³⁶⁾, but it must be remembered that this holds only when no specific adsorption is taking place.

If there is a strong specific adsorption of surface active ions in the Stern layer, we can expect a large shift in the zero point of charge due to the high value of ΔG_+ or ΔG_- ; this leads to the condition $\psi_0^0 \approx 0$ in equation (33). This shift has been observed in experiments on the potentiometric titration of silver iodide suspensions in the presence of surface active agents³⁷⁾.

In these discussions on the zero point of charge we have implicitly assumed constancy of the $\Delta\chi$ potential. The last quantity consists of the potential drop in the solid phase near the boundary and includes also the potential due to orientation of water dipoles, *etc.* The former arises from the lower electrochemical free energy of lattice ions at the surface compared with that in the bulk of the solid phase, overshooting of free electrons³⁸⁾ (in the case of metal surfaces), *etc.* All of these factors are, strictly speaking, not constant for a change in the surface charge, and hence equation (33) is rather qualitative from the theoretical point of view. It must also be mentioned here that $\Delta\chi$ will probably not remain constant, if the interfacial water structure is destroyed, or replaced, by the adsorbed surface active agents.

(ii) Application to the Coated Surface

A typical example of the extension of the concept of an ideal polarised electrode to a solid surface is given by a silver iodide surface coated by surface active agents, *vide* Part 3. It is clear from Fig. 1 (D) that we can consider that the effective surface has shifted to the ψ_0' -plane. On this assumption, the double layer starts from this plane and we can apply the discussions on the structure of the double layer from this plane onwards as used by Grahame. The concept of the potential determining ion loses its meaning at this plane, because the charge σ_0' is completely defined by the amount of the head groups on this plane and the silver ion in the solution no longer behaves as the potential determining ion, *vide* Part 2.

The surface charge is defined by the applied electromotive force in the case of a mercury electrode, and by the surface active agent concentration in the case of covered surface, each giving an extra degree of freedom to the system. In one sense, the latter case is the same in principle as the ideal non-polarisable electrode, inasmuch as the surface charge is defined by an ionic concentration in the solution. This seems to be related to the fact shown by Grahame and Whitney³³⁾ that both types of electrodes lead to the same thermodynamic equation of electrocapillarity. The difference is seen only when the real picture of the electrical double layer is considered.

We have so far defined the surface covered by surface active ions as an ideal polarised electrode. Thus, the adsorbability of the counter ions in the inner Helmholtz plane of this layer becomes strongly dependent on the bond strength between the head groups and these ions. It has been shown in Part 3 that this was really the situation, because the adsorbability was in accord with the solubility.

The author wishes to express his gratitude to Dr. R. H. Ottewill, University of Cambridge, for his kind supervision and continuous advice. Thanks are also due to the British Council for the Scholarship and to the University of Cambridge for the Oliver Gatty Studentship. The author's thanks are also due to Professor I. Tachi

and to Dr. S. Ueda for their continuous interest and encouragement.

REFERENCES

- (1) A. Watanabe, This Bulletin, 38, 158(1960).
- (2) A. Watanabe, This Bulletin, 38, 179(1960).
- (3) A. Watanabe, This Bulletin, 38, 216(1960).
- (4) H. Helmholtz, *Wiss. Abhandl. physik. techn. Reichsanstalt*, 7, 925 (1879).
- (5) L. Gouy, *J. phys.*, (4), 9, 457 (1910) ; *Ann. phys.*, (9), 7, 129 (1917).
- (6) D. L. Chapman, *Phil. Mag.*, (6), 25, 475 (1913).
- (7) P. Debye and E. Hückel, *Physik. Z.*, 24, 184, 305 (1923).
- (8) N. K. Adam, "Physics and Chemistry of Surface," Oxford Univ. Press, London (1941).
- (9) D. C. Grahame, *Chem. Rev.*, 41, 441 (1947).
- (10) P. Debye, "Polar Molecules," Chem. Catalog, New York (1929).
- (11) D. C. Grahame, *J. Chem. Phys.*, 18, 903 (1950).
- (12) F. Booth, *ibid.*, 19, 391, 1327, 1651 (1951).
- (13) B. E. Conway, J. O'M. Bockris and L. A. Ammar, *Trans. Faraday Soc.*, 47, 756 (1951).
- (14) E. J. Verwey and J. Th. G. Overbeek, "Theory of Stability of Hydrophobic Colloids," Elsevier, Amsterdam (1948).
- (15) E. J. Verwey and K. F. Niessen, *Phil. Mag.*, (7), 28, 435 (1939).
- (16) D. C. Grahame, *J. Chem. Phys.*, 21, 1054 (1953).
- (17) J. R. MacDonald, *ibid.*, 22, 1857 (1954).
- (18) J. Kirkwood, *ibid.*, 2, 767 (1934).
- (19) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge Univ. Press, London (1939).
- (20) O. Stern, *Z. Elektrochem.*, 30, 508 (1924).
- (21) I. Langmuir, *J. Am. Chem. Soc.*, 40, 1361 (1918).
- (22) E. Wicke and M. Eigen, *Z. Elektrochem.*, 56, 551 (1952).
- (23) M. Eigen and E. Wicke, *J. Phys. Chem.*, 58, 703 (1954).
- (24) V. Freise, *Z. Elektrochem.*, 56, 822 (1952).
- (25) N. Ise and M. Hosono, *J. Polymer Sci.*, 39, 389 (1959).
- (26) E. A. Guggenheim, *J. Phys. Chem.*, 33, 842 (1929).
- (27) J. J. Bikerman, *Phil. Mag.*, (7), 33, 384 (1942).
- (28) G. H. Bolt, *J. Colloid Sci.*, 10, 206 (1955).
- (29) A. Watanabe, F. Tsuji and S. Ueda, This Bulletin, 33, 91 (1955) ; 34, 1, 65 (1956) ; *Proc. 2nd Intern. Congr. Surface Activity, London*, 3, 94 (1957).
- (30) J. Th. G. Overbeek, *J. Colloid Sci.*, 8, 420 (1953).
- (31) S. R. De Groot, "Thermodynamics of Irreversible Processes", North Holl., Amsterdam (1951).
- (32) R. Defay and P. Mazur, *Bull. Soc. Chim., Belge.*, 63, 562 (1954).
- (33) D. C. Grahame and R. B. Whitney, *J. Am. Chem. Soc.*, 64, 1942 (1942).
- (34) R. Parsons, in Bockris', "Modern Aspects of Electrochemistry," 1, Butterworths, London (1954).
- (35) E. Lange and K. P. Mishchenko, *Z. physik. Chem.*, 149, 1 (1930).
- (36) E. J. Verwey and H. R. Kruyt, *ibid.*, 167, 149 (1933).
- (37) R. H. Ottewill and A. Watanabe, unpublished.
- (38) L. Brillouin, "Die Quantenstatistik," (German Translation), Julius Springer, Berlin (1931).