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THE NOTION OF THE ELECTRODE CHARGE AND THE LIPPMANN EQUATION

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The notion of the electrode charge is one of the fundamental notions of electrochemistry. Its meaning, however, is understood in a different way in different cases. This, in particular, is one of the reasons for the disagreement between the values of potential of zero charge given by various authors, which still remains in spite of many experimental studies carried out recently on the determination of p.z.c.[1-4]. In this connection, we thought it expedient to analyze in more detail this notion as well as the Lippmann equation, which is the main thermodynamic relation containing the charge value.

A customary definition of the charge value is based on the concept of the existence of the electric double layer at the metal/electrolyte interface. The electrode charge is assumed to be identical with the charge of the metal side of the double layer. In this case the charge value and, hence, that of p.z.c., depends on the electric double-layer model used.

IDEAL POLARIZED ELECTRODE

Let us consider first the case of an ideal polarized electrode on whose surface there is no transfer of charged particles from one phase to another. The charge of the metal side of the double layer Q is equal in absolute value and opposite in sign to the charge of its ionic side:

$$Q = -\Sigma\Gamma_i + \Sigma\Gamma_j \tag{1}$$

where Γ_i is the Gibbs adsorption of the cations and Γ_j the same of the anions of the solution forming part of the ionic side of the electric double layer; the quantities Γ_i and Γ_j are expressed in C cm^{-2} in accordance with the ion charge values in the solution bulk. The value of Q in eqn. (1) does not depend on the location of the interface. Here and below, unless otherwise specified, we shall assume that its location is determined by the condition $\Gamma_{H_2O} = 0$. For Q in eqn. (1) to express correctly the charge of the metal side of the double layer it is necessary that the value of the charge of the particles adsorbed should not vary during their adsorption. However, according to Lorenz[5,6], a major part of the charge of the double-layer ions on Hg and liquid Ga is transferred to the electrode, in the case of the alkali metal cations also. Although the method suggested by Lorenz for the determination of the fraction of the charge transferred is open to objection[7], the possibility of such transfer is unquestionable in principle*. To deny this would be to assert that there is no covalent bonding between the electrode and the double-layer ions. Such points of view have been expressed[8] but cannot be considered as being proved.

The notion of the "ideally polarized" electrode has been widely used in modern electrochemical literature[9-13] and has served as a basis for the development of the quantitative theory of the double layer. Many of the conclusions of this theory have been experimentally confirmed, the relevant data having been obtained mainly for the mercury electrode. In this case, if it is assumed that Lorenz's results can be interpreted differently, the concept of the electrode charge based on the modelling of the metal/electrolyte interface by means of the electric double-layer theory could be considered adequate. At present, however, there is considerable experimental material available on the structure of the metal/electrolyte interface for platinum metals which shows that here the case is different, since there is no doubt that charge transfer occurs during the adsorption of most ions on platinum[14-18]. In the presence of such transfer, the determination of the value of the electrode surface charge would require detailed information on the nature of the interaction between the adsorbed ion and the surface, which is not at our disposal at present. Therefore the p.z.c. value also is undetermined.

Beginning with the very first studies on the platinum/electrolyte interface it has been assumed that along with adsorbed ions, adsorbed hydrogen and oxygen atoms[19,20] (or even these alone[21]) are present at the metal/electrolyte interface. Let us consider from this point of view the behaviour of the platinum electrode in a solution 1 *M* with respect to K^+ and Cl^- ions and 0.01 *M* with respect to H^+ ion, confining our study to the potential range 0.15–0.6 V *versus* the reversible hydrogen electrode in the same solution (practically a wider potential range could be used). Under the condition $[H^+] \ll [K^+]$ it is reasonable to assume that the H^+ ion content in the ionic side of the double layer can be neglected[15,22,23] and the H^+ ion adsorption observed depends only on their transition to adsorbed H atoms or *vice versa*. Under this assumption, p.z.c. in the system under consideration[23,24], determined by the condition $\Gamma_{K^+} = \Gamma_{Cl^-}$, is 0.04 V**.

Under the assumption that the transition ion$\rightleftarrows$atom on the electrode surface is realised, the electrode in question cannot be considered as being ideally polarized. However, a different interpretation is formally possible. In the above potential range the concentration of dissolved molecular hydrogen H_2 is small enough (of the order of 10^{-9} *M* or less) for H_2 not to be considered as a solution component. When platinized electrodes are used, the total amount of hydrogen dissolved in the solution bulk can easily be rendered small compared to the amount adsorbed on the electrode surface. Thus, if a platinized electrode with visible surface 4 cm^2 and true surface 4000 cm^2 is in equilibrium with 1 cm^3 of solution, which corresponds to the actual conditions of our experiments, at a potential differing by 0.15 V from the reversible hydrogen potential in the same solution, the amount of hydrogen dissolved is of the order of 10^{-12} moles and of hydrogen adsorbed of the order of 10^{-6} moles. Under these conditions, we can vary the electrode potential practically without changing

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[*] Capacity measurements show unambiguously that in the case of a flat orientation of the benzene ring there occurs a charge transfer from a positively charged mercury electrode on adsorbed molecules of aromatic compounds[60-62].

[**] Unless otherwise specified, potentials are referred to NHE.

the composition of the bulk phases of the system. In other words, the electrode posesses that additional degree of freedom which is characteristic of ideal polarized electrodes[12]. The maximum density of the stationary current, which under the above conditions can flow from the electrode surface to the bulk of the solution, previously freed of H_2, in the absence of forced stirring is no more than 10^{-8} A cm^{-2} of geometric surface of the electrode. Thus, the requirement for impossibility of steady current flow in the case of ideal polarizability of the electrode[10] also proves to be practically satisfied. Finally, following this approach, it could be supposed that H^+ ions, strongly adsorbed as they are, retain their ionic nature. In this case, p.z.c. is determined by the condition $\Gamma^s_{H^+}+\Gamma_{K^+}=\Gamma_{Cl^-}$, which leads to the value[22,24] of p.z.c. 0.14 V*. Such treatment of the Pt–H electrode is unusual** and some objections could be raised against it. Thus, for example, if we considered all adsorbed hydrogen ions to retain their charge, we should arrive at large values of the surface charge which are inconsistent with the usual picture of the electric double layer. The platinum charge in a solution of the composition mentioned at $\varphi=0.04$ V would not be zero but -32 μC cm^{-2}, and at the reversible hydrogen potential in its absolute value would be greater than 200 μC cm^{-2}. Evidently such an argument cannot, however, be taken into consideration in a thermodynamic treatment of the problem, within the framework of which the adsorbed H atom and the pair: electron on the metal and H^+ ion drawn from the solution bulk—are completely equivalent.

Further difficulties, which have been sufficiently discussed in earlier studies, arise when we consider ionic adsorption on Pt from solutions containing strongly adsorbed cations such as Cd^{2+} and Tl^+ [14,15,18,26]. The behaviour of adsorbed Cd^{2+} and even to a greater extent that of Tl^+, testifies to their bond with platinum being mainly covalent. It is possible that they form a surface alloy with Pt[15,27]. In this case, the charge of the ions being adsorbed should be considered as belonging to the metal side of the double layer rather than to the ionic side. Thus, in the presence of strong chemisorption processes, the determination of the values of the charge and p.z.c. of the Pt electrode in the usual sense of these terms becomes impossible. To a certain approximation it can be carried out for such ions as SO_4^{2-} anions and Li^+, Na^+ and K^+ cations, which are rather weakly adsorbed on Pt. Similar difficulties arise in the case of halogen ion adsorption on metals of the iron group[28].

It follows that it is necessary to differentiate between the two definitions of the term "charge"[15,22,29,30], one of which refers to the quantity contained in thermodynamic relations and the other to the charge of the metal side of the double layer, modelling to a certain approximation the charge distribution at the given interface. The thermodynamic studies of reversible electrodes have long shown the necessity

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* The superscript s in Γ_{H^+} has been added to distinguish this value of Γ_{H^+} from that ascribed to Γ_{H^+} in our earlier studies. In ref. 29 the quantity $\Gamma^s_{H^+}$ is written as $(\Gamma_{H^+})_\varphi$.

** The statement that such treatment is possible is made here in order to prove the necessity of giving to the notion of the electrode charge a definition which would be independent of the concepts of the double-layer structure. In fact, the information available on the platinum–hydrogen electrode shows that it is reasonable to distinguish in the surface layer between adsorbed hydrogen ions and adsorbed hydrogen atoms[15,22,23]. In accordance with this, in our earlier studies on this problem we pointed out that the platinum hydrogen electrode is not an "ideally polarized", but only a "completely polarizable" one in Planck's sense[25], *i.e.* an electrode whose state is completely determined by the quantity of electricity passed through it since a certain moment of time. However, as has been shown above, in terms of a purely thermodynamic treatment it can also be called "ideally polarized".

to take account of this difference[31,32]. With reference to the theory of the ideally polarized electrode, this was first pointed out by Lorenz[5]. We would think it suitable to call the former quantity—the total, or thermodynamic, and the latter—the free charge of the electrode surface. Lorenz calls the former quantity "conventional" charge[5]. The justification of the use of the term "total" charge will be evident from what follows. Henceforth we shall designate the former quantity by Q and the latter by ε.

In the case of an ideally polarized electrode the value of Q is equal to the right-hand side of eqn. (1), if all Γ_i and Γ_j are taken into consideration regardless of the form in which the charged solution components pass into the surface layer*. If all the remaining metal phase components are considered to be uncharged, which is always admissible, the quantity Q in the left-hand side of eqn. (1) can be equated with Gibbs adsorption of electrons with a minus sign

$$Q = -\Gamma_e$$

The total charge of an ideally polarized electrode can be also defined in a different manner, preserving completely the analogy with an ordinary capacitor, *viz.* as the quantity of electricity to be supplied to the electrode when its surface is increased by 1 cm^2, so that the potential difference electrode/solution should remain constant, keeping constant also the chemical potentials of all the solution components (both charged and uncharged) as well as the metal phase components. Such definition of the charge has already been given by Lippmann[33,34], who called this quantity "electrode capacity at constant potential". Lippmann, however, did not mention the necessity of keeping constant not only the electrode potential, but also the chemical potentials of all system components. Evidently, in the case of an ideally polarized electrode the value of Q thus determined is identical with the left-hand side of eqn. (1).

The derivation of Lippmann's equation for an ideally polarized electrode has been considered repeatedly in the literature[9-13] and we need not return to it here. It should be noted, however, that usually the difference between Q and ε has not been taken into account. It is clear already from Lippmann's derivation that this equation should be written as:

$$\partial\sigma/\partial\varphi = -Q \tag{2}$$

where σ is the free surface energy (in the case of a liquid metal it is the interfacial tension as well) and φ the electrode potential measured *versus* a constant reference electrode. The fact that in the case of an ideally polarized electrode the right-hand side of eqn. (2) contains Q and not ε was emphasized by Lorenz[5].

THE PLATINUM–HYDROGEN ELECTRODE TREATED AS A REVERSIBLE ELECTRODE

The determination of the total charge value from eqn. (1) is evidently inapplicable to a reversible electrode due to the possibility of charge transfer through the interface. Let us show that the second determination, which should be called after

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* In the case of an ideally polarized electrode the adsorption of uncharged components does not introduce any terms into Q.

Lippmann, can be extended under definite conditions to reversible electrodes as well. With such treatment, the difference between the cases of ideally polarized and reversible electrodes consists in the following. As has already been stated, for the case of an ideally polarized electrode, in order to keep the system state constant, when the surface is increased by 1 cm^2, it is necessary to introduce, apart from the quantity of electricity Q, the quantities Γ of all independent solution components and similar quantities for the metal phase (Gibbs adsorption values). In the case of a reversible electrode, there are components whose concentrations at a given electrode potential and fixed concentration of the other components, are automatically maintained constant, as for example, the H_2 concentration in the case of a platinum–hydrogen electrode in a solution containing H^+ ions in a given concentration. Further, the surface layer of a reversible electrode can be formed of uncharged components only, without supply of electricity from outside, since free charges of the double layer can be produced by the electrode process. We shall use this possibility.

The Gibbs equation for the reversible system consisting of the components H, HA and CA can be given the form

$$d\sigma = -\Gamma_{H} d\mu_{H} - \Gamma_{CA} d\mu_{CA} - \Gamma_{HA} d\mu_{HA} \tag{3}$$

The chemical potentials μ and the adsorption Γ are expressed in electrical units (μ in volts, Γ in C cm^{-2}). We do not take water into consideration, as $\Gamma_{H_2O} = 0$.

Equation (3) can also be written in the form:

$$d\sigma = -\Gamma_{H} d\mu_{H} - \Gamma_{H^+} d\mu_{H^+} - \Gamma_{C^+} d\mu_{C^+} - \Gamma_{A^-} d\mu_{A^-} \tag{4}$$

since

$$\Gamma_{H^+} = \Gamma_{HA} \tag{5}$$

$$\Gamma_{C^+} = \Gamma_{CA} \tag{6}$$

and

$$\Gamma_{A^-} = \Gamma_{HA} + \Gamma_{CA} \tag{7}$$

The quantities Γ_H and Γ_{H^+} are the Gibbs hydrogen adsorptions in atomic and ionic forms, respectively, *i.e.* the amounts of hydrogen atoms and ions to be added to the system when the interface area increases by 1 cm^2, for the composition of the bulk phases (and hence the potential difference between them) to remain unchanged. The quantities Γ_H and Γ_{H^+} include not only the surface excesses of the respective components, but also the amounts of substance which are consumed due to the potential-determining adsorption and which during the formation of the new phase pass from the reduced form into the oxidised form, or *vice versa.* Equations (3) and (4) correspond to the case when the formation of a new surface occurs without supply of electricity from outside; they have already been used in our earlier papers for treatment of the thermodynamics of the Pt–H system[16,17,29,35] and have been confirmed by numerous measurements.

Let us transform eqns. (3) and (4) in such a way that it should be possible to use them under other conditions of the new surface formation, introducing the value φ_A for the potential of the hydrogen electrode measured against an electrode reversible with respect to the A^- anion in the same solution. There exists an obvious relation between the quantities $d\mu_H$, $d\mu_{H^+}$, $d\mu_{A^-}$ and $d\varphi_A$:

$$d\mu_{H^+} - d\mu_H = d\varphi_A - d\mu_{A^-} \tag{8}$$

or

$$d\mu_{HA} = d\varphi_A + d\mu_H \tag{9}$$

Using eqns. (5) and (9), we obtain from (3), (4), (6)–(8) two relations

$$d\sigma = \Gamma_H d\varphi_A - \Gamma_{CA} d\mu_{CA} - (\Gamma_H + \Gamma_{H^+}) d\mu_{HA} \tag{10}$$

and

$$d\sigma = -(\Gamma_H + \Gamma_{H^+}) d\mu_H - \Gamma_{CA} d\mu_{CA} - \Gamma_{H^+} d\varphi_A \tag{11}$$

Let us consider first eqn. (10). According to eqn. (10)

$$(\partial\sigma/\partial\varphi_A)_{\mu_{HA},\mu_{CA}} = \Gamma_H = -Q' \tag{12}$$

If we proceed from the charge determination discussed above, the quantity $Q' = -\Gamma_H$ can be treated as the total electrode charge and, hence, eqn. (12) as the Lippmann equation under the condition $\mu_{HA} = \text{const}$. Indeed, let us, when the electrode surface is increased by 1 cm^2, introduce into the system the charge $Q' = -\Gamma_H$ and compensate for the change in the hydrogen content in the bulk phases by adding hydrogen in the amount $\Gamma_H + \Gamma_{H^+}$ in the form of hydrogen ions. As the result of interaction with the introduced charge, Γ_H ions will change to atoms and thus the composition of the system will be restored, assuming that the constancy of the quantities μ_{C^+} and μ_{A^-} is ensured by introduction into the solution of C^+ and A^- in the amounts Γ_{C^+} and Γ_{A^-}, respectively.

It can be readily shown, however, that in the case of a reversible system the choice of the quantity which we identify with the total electrode charge is not unambiguous. In fact, it follows from (11) that

$$(\partial\sigma/\partial\varphi_A)_{\mu_H,\mu_{CA}} = -\Gamma_{H^+} = -Q'' \tag{13}$$

The quantity Γ_{H^+} can also be treated as the total electrode charge if the change in the hydrogen content in the system with increasing surface is compensated for by addition of the same amount of hydrogen $\Gamma_H + \Gamma_{H^+}$, but as atoms rather than as ions. As the result of interaction with the charge $Q'' = \Gamma_{H^+}$, Γ_{H^+} atoms will change to ions, *i.e.* Γ_H hydrogen atoms and Γ_{H^+} hydrogen ions will be introduced into the system, which will lead to the restoration of the initial composition. Equation (13) is a Lippmann equation, but under the condition $\mu_H = \text{const}$. In this case the variation of the potential of the Pt–H electrode is determined by the variation of [HA]. In order to assure under these conditions the constancy of the reference electrode, the ratio [HA]/[CA] should be kept small.

Now let us consider the physical significance of $Q' = -\Gamma_H$ and $Q'' = \Gamma_{H^+}$ making use of a certain surface-layer model and of some non-thermodynamic quantities. We shall thus assume that there are free charges on the surface whose density is ε and that hydrogen is present in two forms: as adsorbed atoms and as adsorbed ions, and that, finally, there is no partial charge transfer to the electrode from A^- and C^+ ions. The surface excesses of hydrogen in the two forms we shall denote by A_H and A_{H^+}, respectively*. The quantity Γ_H is equal to the Gibbs adsorption of hydrogen and includes both the surface excess of hydrogen in the atomic form A_H

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* In refs. 16, 17 and 23 the quantity A_{H^+} was denoted by $\Gamma^i_{H^+}$.

and the amount of hydrogen atoms which pass to H^+ ions when 1 cm^2 of interface is formed, leaving the charge ε at the interface. Thus,

$$-(\partial\sigma/\partial\varphi_A)_{\mu_{HA},\mu_{CA}} = Q' = -\Gamma_H = \varepsilon - A_H \tag{14}$$

Equation (14) gives the value of the charge of the reversible electrode under the condition μ_{HA}=const. when the surface layer is formed from the charge Q' and hydrogen ions in the amount $\Gamma_H+\Gamma_{H^+}$*.

Similarly, the quantity Γ_{H^+} is made up of A_{H^+}, the surface excess of H^+ ions, and the amount of hydrogen ions which change to atoms when new surface is formed, imparting to the surface the charge ε. Thus,

$$-(\partial\sigma/\partial\varphi_A)_{\mu_H,\mu_{CA}} = Q'' = \Gamma_{H^+} = \varepsilon + A_{H^+} \tag{15}$$

Equation (15) gives the value of the charge under the condition μ_H=const., when the surface layer is formed of the charge Q'' and hydrogen atoms in the amount $\Gamma_H+\Gamma_{H^+}$**. If we specify our model further by assuming that the H^+ ions, whose surface excess determines the value of A_{H^+}, from part of the ionic side of the double layer, A_{H^+} must vanish in the presence of a sufficient excess of foreign cations, and the total charge Q'' becomes equal to the free charge ε.

It follows from (14) and (15) that

$$\Gamma_H+\Gamma_{H^+} = A_H + A_{H^+} = \Gamma^s_{H^+} \tag{16}$$

Thus, though A_H and A_{H^+}, taken separately, are non-thermodynamic quantities, $A_H+A_{H^+}$ is equal to the thermodynamic quantity $\Gamma_H+\Gamma_{H^+}$ and gives the overall Gibbs adsorption of the reduced and oxidised components of the reversible redox system H,H^+.

It follows from the foregoing that the Lippmann determination of the value of Q, equal to $-\partial\sigma/\partial\varphi$, is valid for reversible systems as well, but the value of Q proves to be dependent on which chemical potential we keep constant with varying electrode potential: that of the reduced or that of the oxidized component. However, it is possible to set also other conditions on the chemical potentials or concentrations of the reduced and oxidised components when varying the electrode potential. By choosing a proper ratio between the part of the total adsorption which is introduced as the oxidised component and that which is introduced as the reduced component, it is possible to ensure the validity of the Lippmann equation and to treat therefore the quantity $-\partial\sigma/\partial\varphi$ obtained from the Gibbs adsorption equation as the electrode charge in accordance with the definition of this notion given by us. An example will be given below. It would be possible to obtain thus an infinite number of charge values and electrocapillary curves for a given redox system. However, in addition to the validity of eqn. (4), the simplicity of the conditions of the electrode-potential variation proposed here, there is one more argument in favour of choosing the total

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* In the experimental determinations of the thermodynamic quantity Γ_H carried out so far, use was made of the assumptions concerning the double-layer structure at the platinum/solution interface, which are beyond the scope of thermodynamics[22,24]. However, a determination of Γ_H independent of such assumptions is in principle possible although presenting experimental difficulties. It should be based on adsorption measurements on a platinum electrode previously degassed *in vacuo*.

**From eqns. (3), (5), (14) and (15) at [CA] = const. we obtain the noteworthy relation:

$$d\sigma = (\varepsilon - A_H)d\mu_H - (\varepsilon + A_{H^+})d\mu_{H^+} \tag{3a}$$

charge values suggested by us. Indeed, the charge value Q', determined as $-\Gamma_H = \varepsilon - A_H$, expresses with an opposite sign the amount of negative electricity that can be drawn off from 1 cm^2 of electrode surface (the exchange between the electrode and the solution bulk being stopped) when the electrode-surface layer is completely oxidised, *i.e.* a surface layer is obtained which can be built, according to eqns. (3a) and (4), of the oxidised form H^+ without supply of H atoms and of electricity from outside. Similarly, the charge Q'', determined as $\Gamma_{H^+} = \varepsilon + A_{H^+}$, represents the amount of positive electricity to be drawn from 1 cm^2 of electrode surface at complete reduction under the same condition. Thus, the definition of the "charge" given here[22] is a two-dimensional analogue to the definition of the electrode charge in a cell generally accepted in applied electrochemistry. This confirms the main conclusion of the present study, *viz.* that with a rational definition of the notion "charge" the Lippmann equation is valid not only for ideally polarized, but for reversible electrodes as well. Therefore, we cannot agree with the statement made in ref. 36 that the Lippmann equation does not exist for a reversible system.

In our earlier studies the values of $\varphi_{Q=0}$ for a platinum–hydrogen electrode were given corresponding to both methods of potential variation: $\varphi_{\Gamma_H=0}$ and $\varphi_{\Gamma_{H^+}=0}$[16,22,24,29,30,37]. Thus, for Pt in 0.01 *N* HCl+1 *N* KCl, $\varphi_{\Gamma_H=0} = 0.14$ V, and $\varphi_{\Gamma_{H^+}=0} = 0.04$ V. We called the former quantity the potential of the zero total charge and the latter the potential of the zero free charge. The last mentioned definition, however, is only roughly correct, *viz.* with that degree of accuracy with which it is possible to assume $A_{H^+} = 0$ and to ignore the chemisorptive interaction with the electrode surface of all solution ions, except H^+ ion. More exactly $\varphi_{\Gamma_{H^+}=0}$ is the potential of the zero total charge at $\mu_H = \text{const.}$, and $\Gamma_{H^+} = \Gamma_{A^-} - \Gamma_{C^+}$*.

In the treatment of the platinum–hydrogen electrode given here we proceeded from eqn. (3), considering this electrode as being a reversible one. As is shown in ref. 29a the same final results can be arrived at on the basis of the equation

$$d\sigma = -Q\,d\varphi_A - \Gamma_{C^+}\,d\mu_{CA} - \Gamma^s_{H^+}\,d\mu_{HA} \qquad (17)$$

valid for an ideally polarized electrode[11-13], where Q is the total charge of the electrode surface, Γ_{C^+} and $\Gamma^s_{H^+}$ the Gibbs adsorptions of C^+ and H^+ ions and φ_A the potential measured *versus* a reference electrode reversible with respect to A^- anions. However, when passing from eqn. (17) to eqn. (3), it is necessary to introduce non-thermodynamic quantities, *e.g.* ε and A_H,which we avoided here before the introduction of model concepts of the surface-layer structure.

METAL ELECTRODES IN A SOLUTION CONTAINING METAL IONS

In many cases the choice between the two above mentioned methods of variation of the electrode potential of a reversible redox system is determined by the question of which of the chemical potentials of its components it is more convenient

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* The p.z.c. values of platinum given here are greatly at variance with those obtained by Bockris and collaborators[3]. We shall not dwell here on the reasons for this discrepancy, since the values given in ref. 3 as stated by the authors refer to a non-activated platinum electrode free from hydrogen, whereas the main prerequisite of the present study is the establishment of the H,H^+ equilibrium, which was achieved by platinization of the electrode and anodic–cathodic activation. We expect to return elsewhere to the question of the interpretation of the p.z.c. values obtained in ref. 3.

to keep constant. Let us consider from this point of view the system Hg, Tl, C$^+$, A$^-$, H_2O, where Tl can be present both as Tl$^+$ ions and as atoms dissolved in mercury. We shall confine our study to the potential range in which the appearance of mercury ions in the solution can be neglected and to Tl$^+$ and C$^+$ concentrations low enough for μ_{H_2O} to be assumed constant. In this case it is convenient to locate the interface assuming $\Gamma_{Hg}=0$. Under these assumptions, the system in question can be considered as consisting of the components Tl, TlA and CA and treated in the same way as we treated the system composed of H, HA and CA. In accordance with (13), the following relation is valid

$$d\sigma = -\Gamma_{Tl}d\mu_{Tl} - \Gamma_{CA}d\mu_{CA} - \Gamma_{TlA}d\mu_{TlA} \tag{18}$$

From (18) it is easy to obtain, as we have obtained eqns. (10), (11), (14), (15) and (16), the following equations:

$$\begin{aligned} d\sigma &= -(A_{Tl}+A_{Tl^+})d\mu_{Tl} - \Gamma_{CA}d\mu_{CA} - \Gamma_{Tl^+}d\varphi_A \\ &= -(A_{Tl}+A_{Tl^+})d\mu_{Tl} - \Gamma_{CA}d\mu_{CA} - (\varepsilon + A_{Tl^+})d\varphi_A \end{aligned} \tag{19}$$

$$(\partial\sigma/\partial\varphi_A)_{\mu_{TlA},\mu_{CA}} = -Q' = \Gamma_{Tl} = A_{Tl} - \varepsilon \tag{20}$$

$$(\partial\sigma/\partial\varphi_A)_{\mu_{Tl},\mu_{CA}} = -Q'' = -\Gamma_{Tl^+} = -\varepsilon - A_{Tl^+} \tag{21}$$

where A_{Tl} is the amount of Tl present in the surface layer as atoms and A_{Tl^+} the amount of adsorbed Tl$^+$ ions remaining in the ionic side of the double layer, *i.e.* not giving up their charge to the electrode surface.

Now let us consider in terms of the foregoing the processes occurring during cathodic polarization of Hg in a solution containing Tl$^+$ ions. As long as the change of [Tl$^+$] resulting from the formation of Tl amalgam during cathodic polarization of the electrode is small, the condition $\mu_{TlA}=$const. is approximately fulfilled. In this case the dependence of σ of a mercury electrode on φ_A in a TlA+CA solution is determined by eqn. (20), which can be considered as the Lippmann equation of the electrocapillary curve of mercury in this solution*. Such curves have been obtained a number of times[38-41], it being assumed in their treatment that the quantity A_{Tl} could be neglected, *i.e.* the electrode was considered as an ideally polarized one, taking account of the specific adsorption of Tl$^+$ ions only**. According to Lorenz[6], however, part of the charge of Tl$^+$ ions is transferred to mercury, this being equivalent to the assumption of a finite value of A_{Tl} in eqn. (20). At sufficiently negative potentials, thallium practically completely passes into the amalgam, the Tl$^+$ concentration in solution becomes negligible, and μ_{Tl} a constant. In this potential range the electrocapillary curve of the electrode obeys eqn. (21) and the total electrode charge has a different value, which in eqn. (21) is indicated by the substitution of the symbol Q' for Q''. In the presence of an excess of C$^+$ ions, the quantity A_{Tl^+} at sufficiently negative potentials can probably be neglected and the electrode behaviour treated as that of an

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* It has already been pointed out in ref. 31 that in the case of amalgam formation resulting from the discharge of the solution cations, the right-hand side of the Lippmann equation, along with the term taking account of the charge, must contain a term taking account of the adsorption of atoms of the metal forming the amalgam.

** It follows from refs. 39–41 that in the presence of complexing anions, Tl$^+$ is adsorbed on mercury primarily in the form of anion complexes. The quantity which we denoted by A_{Tl^+}, includes the total amount of Tl$^+$ in the ionic side of the double layer, regardless of the form in which thallium ions are adsorbed.

ideally polarized Tl amalgam electrode[41a] if, of course, we do not consider the possibility of the discharge of K^+ ions. Thus, it follows from the treatment of the electrocapillary behaviour of the reversible system given here that in this system it is possible to obtain two kinds of electrocapillary curves. As is clear from Fig. 1, taken from the papers by Frumkin and Polianovskaya[39,40], two electrocapillary curves were actually obtained during cathodic polarization of a mercury electrode in an acidified 0.2 *N* $TlNO_3 + 0.8$ *N* KNO_3 solution. Although in this case the measurements were carried out under conditions which do not correspond to the assumptions of the thermodynamic approach, *viz.* in the range of sufficiently negative potentials when appreciable current passed through the system and there existed concentration gradients of thallium in the amalgam and of Tl^+ ions in the aqueous phases, the results obtained can serve as a qualitative illustration of the correctness of this approach.

The steep rise of the σ,φ curve at φ values in the range 0.50–0.55 V *vs.* NCE indicates according to eqn. (21) that in this potential range the quantity A_{Tl^+} still retains a large positive value, notwithstanding the decrease of the Tl^+ concentration in the solution*.

It should be noted that such distinct separation of the two electrocapillary curves of a redox system, as shown in Fig. 1, is possible only if the difference between the values of $\varphi_{Q'=0}$ and $\varphi_{Q''=0}$ is large. Thus, it is not observed in the case of cathodic polarization of mercury in solutions of cadmium salts[39], though the adsorption behaviour of Cd^{2+} and Tl^+ ions is in many respects similar.

Let us consider in more detail the relation between Q and ε and the form of the Lippmann equation for the common case when the metal phase composition is given. Here, according to (15) and (21), we can write

$$\partial\sigma/\partial\varphi = -Q = -\Gamma_{Me^{n+}} = -\varepsilon - A_{Me^{n+}} \tag{22}$$

where $\Gamma_{Me^{n+}}$ is the total adsorption of Me^{n+} ions and $A_{Me^{n+}}$ the fraction of Me^{n+} ions disappearing from the solution when a new surface is formed without electricity supplied from outside, which remains in the ionic side of the double layer and does not give up its charge to the metal surface. When the anionic composition of the

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* At sufficiently negative potentials, a thallium amalgam electrode in a KNO_3 solution is practically an ideally polarized one. A derivation of the Lippmann equation for this kind of electrode on the basis of the Gibbs equation for a reversible system was given in an early paper by Frumkin, where the case of the mercury electrode was discussed[31]. This derivation was later criticized, it being mentioned, in particular, that in the case under consideration the Hg^{2+} ion concentrations at not very positive potentials are vanishingly small[11,42]. This criticism would be justified if it were the kinetics of the double-layer formation that were being considered, but it cannot affect the correctness of the derivation of the equilibrium conditions.

Although the treatment of the platinum–hydrogen electrode as an ideally polarized one has been shown to be possible in the present paper, one would hardly dispute the validity of treating the system Pt, H_2, H^+ as a reversible one in the potential range indicated, for the reason for example that at the potential 0.48 *versus* the hydrogen electrode in the same solution, H_2 concentration in solution drops to 10^{-20} mol l^{-1}.

The concept of the ideally polarized electrode made the derivation of the basic electrocapillarity equation more elegant, but later excessive contrasting of ideally polarized and reversible electrodes led to erroneous conclusions, such as for example the assumption of the existence in the case of reversible electrodes of a Billiter p.z.c., different from the Lippmann p.z.c., characteristic of ideally polarized electrodes[44,44a,45]. Actually, making an ideally polarized mercury electrode reversible (if this is achieved by introducing sufficiently small amounts of a more electronegative component) has been shown experimentally to have no effect on the electric double-layer structure[45].

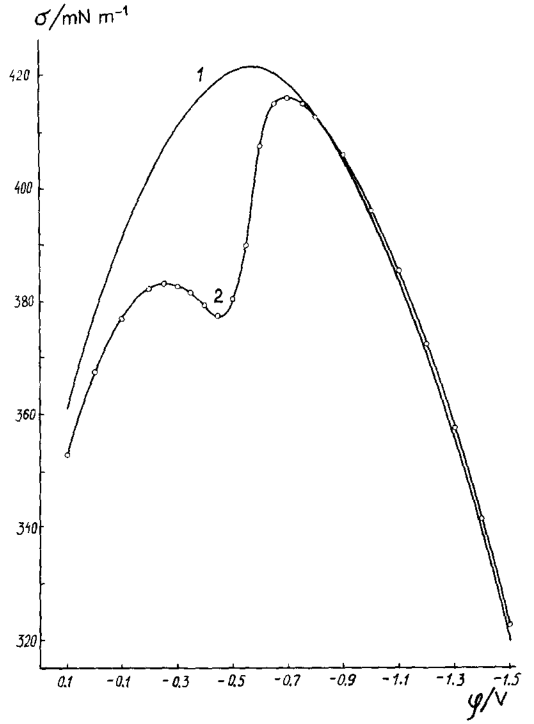

Fig. 1. Dependence of interfacial tension on potential (*vs.* NCE): (1) mercury–1 *N* KNO_3, (2) mercury–0.2 *N* $TlNO_3$ + 0.8 *N* KNO_3[39].

solution is constant, the subscript below $\partial\sigma/\partial\varphi$ can be dropped, since the potential of the reference electrode, reversible with respect to anion, remains constant and the quantity φ can be referred to any constant reference electrode. As has been already pointed out, the introduction of the non-thermodynamic quantity ε into eqn. (22) is justified only under the assumption that there are no covalent bonds between the metal surface and the ions of the ionic side of the double layer.

It has long been understood that what we now call the total and free charges in the case of reversible mercury and amalgam electrodes are different, though it has not been formulated in these terms. Already Krüger[46], to explain the asymmetry of the electrocapillary curve in solutions containing halogen ions, has suggested that on a positively charged mercury surface complex mercury anions are adsorbed and form part of the ionic side of the double layer. Krüger gave Lippmann's equation the form

$$\partial\sigma/\partial\varphi = \varepsilon + F(k-1)c\delta \tag{23}$$

where c is the mercury concentration in solution, k the distribution coefficient of mercury salt between the surface layer and the bulk of the solution and δ the surface layer thickness; the potential was read from solution to electrode.

The assumption of a direct relationship between the second term of the right-hand side of eqn. (23) and the asymmetry of the electrocapillary curve was erroneous[31], but does not however, affect the thermodynamic validity of Krüger's conclusion[34]*. If we consider as adsorbed only the ions which do not give up their charge to the metal surface, and express adsorption in mol cm^{-2}, eqn. (23) can be written as

$$\partial\sigma/\partial\varphi = -\varepsilon - n\Gamma_{\mathrm{Me}^{n+}}F \tag{24}$$

(ε—the "charge", actually the free charge), which coincides with eqn. (22).

Equation (24) was, apparently, first given in this form in ref. 31. Much later it was again derived by Mohilner[47] as an "analogue of Lippmann's classical equation for an ideally polarized electrode in the case of a reversible electrode". As has been already pointed out[34], this formulation is not justified historically.

The electrocapillarity equations for the interface between metal and solution containing metal ions were recently considered once more by Plieth and Vetter[36,48]. It can be readily shown that the differences between the relations derived by these authors and the formulae given here and partly in our earlier studies are due to the different symbols used, while actually their mathematical content is the same. Thus for example, in ref. 36 an expression is given (eqn. (29) of the paper quoted) for the case of Zn amalgam in KCl + ZnCl$_2$ solution, which we shall simplify by leaving only the terms essential for the comparison of the two methods of treatment. To this end, we shall put $\Gamma_{\mathrm{H_2O}} = 0$ and $\mu_{\mathrm{KCl}} = \text{const.}$, assume Zn concentration in the amalgam to be small, and [Zn^{2+}] to be small compared with [K$^+$]. After these simplifications the equation under consideration assumes the form

$$\mathrm{d}\sigma = -(\Gamma_{\mathrm{Zn}} - q^{\mathrm{M}}/2F)\mathrm{d}\mu_{\mathrm{Zn}} - (\Gamma_{\mathrm{Zn}^{2+}} + q^{\mathrm{M}}/2F)\mathrm{d}\mu_{\mathrm{Zn}^{2+}} \tag{25}$$

Here Γ_{Zn} and $\Gamma_{\mathrm{Zn}^{2+}}$ are the adsorptions of Zn and Zn^{2+}, and q^{M} the charge (in our understanding of the term the free charge) of the metal surface. In comparing eqn. (25) with the relations derived by us, it should be borne in mind that the quantities Γ in ref. 36 correspond to our A rather than to our Γ** and that the quantities Γ and μ, unlike in the present study, are not expressed in electrical units. Using the symbols of ref. 36 and the relation

$$\mathrm{d}\mu_{\mathrm{Zn}^{2+}} = \mathrm{d}\mu_{\mathrm{Zn}} + 2\,F\mathrm{d}\varphi$$

we obtain from (25)

$$\mathrm{d}\sigma = -(\Gamma_{\mathrm{Zn}} + \Gamma_{\mathrm{Zn}^{2+}})\mathrm{d}\mu_{\mathrm{Zn}} - (q^{\mathrm{M}} + 2\Gamma_{\mathrm{Zn}^{2+}}\,F)\mathrm{d}\varphi \tag{26}$$

Taking into consideration what has been said above about the physical significance and dimensions of the quantities Γ in eqn. (26) as well as the condition $\mu_{\mathrm{KCl}} = \text{const.}$, we see that eqn. (26), which is not derived in ref. 36, is equivalent to our eqn. (19). Just as from eqn. (19), it is possible to obtain from eqn. (26) the electrocapillary curve

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* An assumption, similar to Krüger's, but with a different motivation, was recently made by Barker[43].

** Although the symbol Γ is often used for the surface excesses of reduced and oxidised forms, which we denote by A, in our opinion this use is unjustified. Gibbs' adsorption Γ is a thermodynamic quantity as well as the quantities $\Gamma_{\mathrm{O}} = A_{\mathrm{O}} + \varepsilon$ and $\Gamma_{\mathrm{R}} = A_{\mathrm{R}} - \varepsilon$, but A_{O} and A_{R} are not (O and R for oxidised and reduced forms, respectively). Neither a direct experimental determination of A values under equilibrium conditions, nor a definition of A without the introduction of the concept of the free charge ε, is possible.

equation at $\mu_{\mathrm{Zn}}=\text{const.}$

$$(\partial\sigma/\partial\varphi)_{\mu_{\mathrm{Zn}}} = -(q^{\mathrm{M}}+2\Gamma_{\mathrm{Zn}^{2+}}F)$$

In spite of the identity of mathematical relations, there seems to be a certain difference in the understanding of their physical significance. In fact, it is suggested in ref. 36 that the values of $\Gamma+q^{\mathrm{M}}/zF$, obtained from equations of the type of eqn. (25), can be corrected for the quantity q^{M}/zF by determining q^{M} by means of electrocapillary and capacity measurements, without specifying that this correction is possible only if additional non-thermodynamic assumptions are introduced*.

In ref. 48 Plieth and Vetter consider the case when the reduced and oxidised components of the solution in the adsorbed state are indistinguishable. Following Lorenz's ideas it is assumed that in the adsorbed state the substance carries a charge different from the reduced component charge by the quantity λn, where n is the difference between the charges of the oxidised and reduced components, and $0<\lambda<1$**. Accordingly, in the particular case of a metal electrode in a solution containing ions with the charge z the charge of adsorbed particles is assumed to be equal to λz. For this case Plieth and Vetter derive the electrocapillarity equations (ref. 48, eqn. (54)) which, if all chemical potentials except μ_{M} and $\mu_{\mathrm{M}^{z+}}$ are assumed to be constant and $\Gamma_{\mathrm{H_2O}}=0$, can be presented in the form

$$\mathrm{d}\sigma = -[(1-\lambda)\Gamma_{\mathrm{ad}}-q^{\mathrm{M}}/zF]\,\mathrm{d}\mu_{\mathrm{M}}-[\lambda\Gamma_{\mathrm{ad}}+q^{\mathrm{M}}/zF]\,\mathrm{d}\mu_{\mathrm{M}^{z+}} \tag{27}$$

In this case also, Plieth and Vetter separate the accumulation of the substance adsorbed in the surface layer from the potential-determining adsorption responsible for the charging of the metal side of the double layer, so that the quantities Γ_{ad} should be correlated with our A. Using the Nernst relation

$$\mathrm{d}\mu_{\mathrm{M}^{z+}} = \mathrm{d}\mu_{\mathrm{M}}+zF\,\mathrm{d}\varphi$$

we obtain from (27)

$$\mathrm{d}\sigma = -\Gamma_{\mathrm{ad}}\,\mathrm{d}\mu_{\mathrm{M}}-(q^{\mathrm{M}}+\lambda z\Gamma_{\mathrm{ad}}F)\,\mathrm{d}\varphi \tag{28}$$

The quantity Γ_{ad} represents the total excess of the substance accumulated in the surface layer and corresponds to $(A_{\mathrm{Tl}}+A_{\mathrm{Tl}^+})$ in eqn. (19). According to our terminology, the quantity $q^{\mathrm{M}}+\lambda z\Gamma_{\mathrm{ad}}F$ is the total charge of the electrode surface under the condition $\mu_{\mathrm{M}}=\text{const.}$***, which in eqn. (19) is expressed by the quantity $\varepsilon+A_{\mathrm{Tl}^+}$. Since the term $\lambda z\Gamma_{\mathrm{ad}}F$ gives the value of the charge of the adsorbed particle and we assumed adsorbed Tl (not included in A_{Tl^+}) to be present in the surface layer in uncharged state, in the case under consideration the quantities $\lambda z\Gamma_{\mathrm{ad}}F$ and A_{Tl^+} are identical in their meaning and differ only in the symbols used. Taking into account that the chemical

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* In our understanding, the quantity $q^{\mathrm{M}}+2\Gamma_{\mathrm{Zn}^{2+}}F$ in eqn. (26) is the total electrode charge at $\mu_{\mathrm{Zn}}=\text{const.}$ In the case of an electrode of the platinum–hydrogen type, it is impossible to separate the components of the total charge even by capacity measurements at high frequencies, since on such electrodes the value of q^{M} determined at high frequencies differs from the equilibrium value.

** Unlike Lorenz, Plieth and Vetter denote by λ the fraction of the charge retained on the adsorbed particle, rather than the fraction of the charge transferred to the electrode. In Plieth and Vetter's notation therefore the quantity λ corresponds to the quantity $1-\lambda$ of Lorenz.

*** Under the condition $\mu_{\mathrm{M}^{z+}}=\text{const.}$ the total charge is determined from the expression:

$$\mathrm{d}\sigma = -\Gamma_{\mathrm{ad}}\,\mathrm{d}\mu_{\mathrm{M}^{z+}}-[q^{\mathrm{M}}-(1-\lambda)zF\,\Gamma_{\mathrm{ad}}]\,\mathrm{d}\varphi \tag{28a}$$

potentials of all other solution components were assumed to be constant, in eqn. (19) $d\mu_{CA}=0$ and $d\varphi_A=d\varphi$. Thus, in their mathematical content eqns. (28) and (19) are identical. However, Plieth and Vetter's conclusion, according to which the charge $\lambda z \Gamma_{ad} F$ should be ascribed to the ionic side of the double layer, seems to us to be unjustified, since the problem of ascribing a charge in a reversible redox system to the metal or to the ionic sides of the double layer cannot be solved in terms of a strictly thermodynamic treatment in general, its solution requiring a detailed elucidation of the double-layer structure. Similarly, defining a quantity as the total charge of the electrode is by no means equivalent to saying that this charge actually sits on the metal surface. Also, as is shown in ref. 29a, one can hardly agree with the method of determining λ as proposed in ref. 48.

The case of a Zn amalgam in a Zn salt solution, *e.g.* $ZnSO_4$, is an interesting example of the difference between the free and total charges. The ionic side of the double layer being composed of Zn^{2+} and SO_4^{2-} ions,

$$\varepsilon = -(A_{Zn^{2+}} - \Gamma_{SO_4^{2-}}) \tag{29}$$

where $A_{Zn^{2+}}$ is the fraction of the adsorbed amount of Zn^{2+} ions forming part of the ionic side of the double layer.

In accordance with (21), the total charge Q is

$$Q = \varepsilon + A_{Zn^{2+}} = \Gamma_{SO_4^{2-}} \tag{30}$$

Since at a sufficiently negative potential, negative anion adsorption is small compared to the absolute value of the negative surface charge, according to eqn. (30), the total charge of Zn amalgam in $ZnSO_4$ solution is only a small fraction of the free charge[32]. Subsequently, equations of the type of eqn. (30) were derived anew many times[10,12,36], often using zinc amalgam as an example again. It follows from above that this case illustrates the necessity of distinguishing between free and total surface charges. However, in the case under consideration the difference between these two quantities can be eliminated by adding a sufficient excess of the supporting electrolyte and is of no fundamental importance since we did not assume the existence of covalent bonds in the double layer.

GENERAL CASE OF A REVERSIBLE REDOX SYSTEM

Having discussed two examples of the application of the electrocapillarity theory to reversible systems, we shall confine ourselves now to a brief consideration of the general case of the simplest reversible redox system

$$\mathrm{O} + ne^- \rightleftarrows \mathrm{R} \tag{31}$$

assuming the chemical potentials of all components, except O and R, to be practically constant.

The Nernst equation for such system can be written as

$$d\varphi = d\mu_O - d\mu_R \tag{32}$$

and the Gibbs equation as

$$d\sigma = -\Gamma_O d\mu_O - \Gamma_R d\mu_R \tag{33}$$

where the significance of the symbols Γ, μ and φ remains the same. In expressing the quantities Γ and μ in electrical units, allowance is made for the quantity n from eqn. (31), as is clear from eqns. (34), (35), (43) and (44). The concentrations of O and R should be small as compared with the concentrations of the other solution components in order to make it possible for μ_O and μ_R to vary without affecting the chemical potentials of the other components.

Assuming, in accordance with eqn. (33), that the electric double layer is formed without electricity supply from outside, we obtain for the relation between the charge value and the oxidant particles adsorption the expression

$$\Gamma_O = A_O + \varepsilon \tag{34}$$

and similarly for the adsorption of the reducing agent particles

$$-\Gamma_R = -A_R + \varepsilon \tag{35}$$

where A and ε also have the same significance as before.

At $\mu_O = \text{const.}$, $d\varphi = -d\mu_R$ and $d\sigma = \Gamma_R d\varphi$, whence taking into consideration (35), we find

$$-(\partial\sigma/\partial\varphi)_{\mu_O} = -\Gamma_R = \varepsilon - A_R = Q' \tag{36}$$

where Q', as has been shown earlier, is the total surface charge at constant activity of the oxidant. At $\mu_R = \text{const.}$, $d\varphi = d\mu_O$ and $d\sigma = -\Gamma_O d\varphi$, whence, taking into consideration (34), we find

$$-(\partial\sigma/\partial\varphi)_{\mu_R} = \Gamma_O = \varepsilon + A_O = Q'' \tag{37}$$

where Q'' is the total surface charge at constant activity of the reducing agent*.

According to what has been said above, for such redox systems it is possible to obtain two types of electrocapillary curves: at $\mu_O = \text{const.}$ and at $\mu_R = \text{const.}$ These curves merge only if $A_O = A_R = 0$. The relation between Q' and Q'' follows from eqns. (36) and (37):

$$Q'' = Q' + A_O + A_R \tag{38}$$

In conclusion, it should be emphasized once more that for the sake of simplicity in our treatment of reversible systems we did not allow for the possibility of charge transfers in the adsorbed layer, other than that expressed by eqn. (31). Under that assumption only, can we consider the quantity ε in the equations for the total charge of a reversible electrode as a free charge.

ORGANIC REDOX SYSTEMS

It is of interest to apply the treatment given here to organic redox systems. In a recent study by Plieth[49] on quinone and hydroquinone adsorption on the Hg electrode the equilibrium between the three components

$$QH_2 \rightleftarrows Q + 2\,H^+ + 2e^-$$

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* When considering the redox system Pt,H,H$^+$, we have already discussed the arguments in favour of the treatment of the quantities Q' and Q'' as representing the values of the total charge.

(here Q = quinone) was studied, taking into consideration the intermediate formation of the semiquinone QH. As a result, three relations were obtained (eqns. (13), (14) and (15) *loc.cit.*), which in our notation should be written

$$(\partial\sigma/\partial\mu_{QH_2})_{\mu_Q,\mu_{H^+}} = -A_{QH_2} - \tfrac{1}{2}A_{QH} + \varepsilon \tag{39}$$

$$(\partial\sigma/\partial\mu_Q)_{\mu_{QH_2},\mu_{H^+}} = -A_Q - \tfrac{1}{2}A_{QH} - \varepsilon \tag{40}$$

$$(\partial\sigma/\partial\mu_{H^+})_{\mu_{QH_2},\mu_Q} = -\varepsilon - A_{H^+} \tag{41}$$

However, in the right-hand side of Plieth's eqn. (15), from which eqn. (41) was obtained, the term corresponding to A_{H^+} is omitted under the assumption that this quantity is small compared to ε. This non-thermodynamic assumption, the validity of which we shall not discuss here, makes it possible for Plieth to determine not only the total adsorption $A_{QH_2} + A_{QH} + A_Q$, but also to separate the surface concentrations of the reduced and oxidised components from ε. At μ_{H^+} = const., the left-hand sides of eqns. (39) and (40) become equal to $-(\partial\sigma/\partial\varphi)_{\mu_O}$ and $(\partial\sigma/\partial\varphi)_{\mu_R}$, respectively, and these equations are reduced to the form of eqns. (36) and (37). The introduction of a third variable μ_{H^+} makes it possible to plot one more electrocapillary curve as follows from eqn. (41). In the general case, the number of "characteristic" electrocapillary curves is equal to that of independent variables in the Nernst equation. In ref. 49 the concentration of QH_2, Q and H^+ did not vary widely enough for electrocapillary curves to be plotted.

Now let us consider the electrocapillary dependence obtained if the following relation is fulfilled

$$[O] + \gamma[R] = \text{const.} \tag{42}$$

where γ is a constant. Equation (42) at $\gamma = D_R^{\frac{1}{2}}/D_O^{\frac{1}{2}}$, where D_R and D_O are the diffusion coefficients of the reduced and oxidised forms, respectively, represents the relation between the concentrations of the oxidised and reduced forms at the dropping mercury electrode surface outside the limits of the double layer, if the removal of the substance through adsorption on the drop surface can be neglected. We shall assume that the concentration of hydrogen ions participating in the electrode process is kept constant. Equation (42) also approximates the relation between [O] and [R] under the conditions under which the σ, φ curve of Fig. 1 was obtained.

Since $\mu_O - \mu_R = \varphi - \varphi_{\frac{1}{2}} + \text{const.}$, where $\varphi_{\frac{1}{2}}$ is the potential at which $[O] = \gamma[R]$ (under polarographic conditions the half-wave potential of the electroreduction reaction), it follows from (42) that

$$\mu_O = (\varphi - \varphi_{\frac{1}{2}}) - (RT/nF)\ln[1 + \exp(nF/RT)(\varphi - \varphi_{\frac{1}{2}})] + \text{const.} \tag{43}$$

$$\mu_R = -(RT/nF)\ln[1 + \exp(nF/RT)(\varphi - \varphi_{\frac{1}{2}})] + \text{const.} \tag{44}$$

It follows from (33), (34) and (35) that

$$d\sigma = -(\varepsilon + A_O)d\mu_O + (\varepsilon - A_R)d\mu_R \tag{45}$$

whence, taking into consideration (43) and (44), as well as (36) and (37)

$$\begin{aligned}\frac{\partial\sigma}{\partial\varphi} &= -\varepsilon + \frac{-A_O + A_R\exp(nF/RT)(\varphi - \varphi_{\frac{1}{2}})}{1 + \exp(nF/RT)(\varphi - \varphi_{\frac{1}{2}})}\\ &= -Q'/[1 + \exp(nF/RT)(\varphi_{\frac{1}{2}} - \varphi)] - Q''/[1 + \exp(nF/RT)(\varphi - \varphi_{\frac{1}{2}})]\end{aligned} \tag{46}$$

At $\varphi \gg \varphi_{\frac{1}{2}}$ eqn. (46) changes to eqn. (36), at $\varphi \ll \varphi_{\frac{1}{2}}$—to eqn. (37), *i.e.* to Lippmann's equations corresponding to the conditions $\mu_O = \text{const.}$ or $\mu_R = \text{const.}$*. Equation (46) has already been derived and partly discussed in the literature[51-53], but from a somewhat different point of view. In particular, the quantities which we denote by A_O and A_R have been treated as Gibbs adsorption values.

As can readily be seen, in the case of identical adsorptivity of the O- and R-forms, the second term in the right-hand side of eqn. (46) disappears at all values of φ in the Henry region and at all coverages at $\varphi = \varphi_{\frac{1}{2}}$. If A_R can be neglected at $\varphi > \varphi_{\frac{1}{2}}$ and A_O at $\varphi < \varphi_{\frac{1}{2}}$, the adsorption factors will affect the shape of the σ, φ dependence only through their influence on ε, and the electrocapillary curve corresponding to the differential equation (46) to the first approximation can be composed from two electrocapillary curves of ideally polarized electrodes. However, strong adsorption of R at $\varphi > \varphi_{\frac{1}{2}}$, which is observed in the case of the appearance of prewaves[54] and can be due to the formation of a surface complex RO[55], should lead to a sharp drop of σ. On the contrary, O adsorption at $\varphi < \varphi_{\frac{1}{2}}$ should lead to a rise of σ. Since in the general case the co-adsorption of O and R should occur in a certain potential range including $\varphi_{\frac{1}{2}}$, especially if they form a strongly adsorbed intermediate compound of the type of OR or $\frac{1}{2}$ OR without splitting of the wave, the electrocapillary dependence can be expected to show near $\varphi_{\frac{1}{2}}$ a more or less asymmetrical depression, the shape of which will depend on the effect of the adsorption processes mentioned. In the polarographic literature numerous "electrocapillary curves" are given, that express the dependence of the time of formation or of the weight of a drop on the potential applied to the mercury dropping electrode[54,56-58]. In many cases the shape of these curves confirms the considerations presented here. So far, however, these curves have not been subjected to a thorough theoretical analysis. The possibility of the appearance of two maxima on the electrocapillary curve under polarographic conditions has been pointed out by Barker[43], who, however, does not treat the potential of the second maximum as a p.z.c.**. It seems to us that eqn. (46) can serve as a basis for the interpretation of polarographic "electrocapillary curves"· Unfortunately, σ–φ curves determined from the drop formation time are usually distorted, due to tangential motions of the mercury surface arising during the passage of the current***.

To our knowledge, the only determination of the σ, φ dependence for organic

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* At $\gamma = 1$, eqn. (46) assumes a particularly simply form

$$-\partial\sigma/\partial\varphi = (1-\alpha)Q' + \alpha Q'' \tag{46a}$$

where $\alpha = [\text{O}]/[\text{R}] + [\text{O}]$ is the mole fraction of the oxidised component in the redox system near the electrode surface, but outside the adsorption layer. The right-hand side of eqn. (46a) can be considered as the electrode charge, if we compensate the loss of $A_O + A_R$ in the solution bulk with the surface increase by unity introducing $(1-\alpha)(A_O + A_R)$ in the O-form and $\alpha(A_O + A_R)$ in the R-form. This would be, however, a rather artificial choice.

** The potential of the right-hand side maximum of the polarographic electrocapillary dependence φ_{II} according to eqn. (46) can be treated as a potential of zero total charge if the quantity $(nF/RT)(\varphi_{II} - \varphi_{\frac{1}{2}})$ has a large negative value. In the case of a large positive value of $(nF/RT)(\varphi_I - \varphi_{\frac{1}{2}})$ a similar conclusion can be drawn concerning the potential of the left-hand side maximum φ_I. It is easy to show that there exists a point of zero free charge ($\varepsilon = 0$) in the neighbourhood of $\varphi_{\frac{1}{2}}$ if $A_O \sim A_R$ at $\varphi = \varphi_{\frac{1}{2}}$ and the minimum of the σ–φ curve, as on Fig. 2, corresponds approximately to $\varphi = \varphi_{\frac{1}{2}}$.

***The quantity $A_R - \varepsilon$ obtained from eqn. (46) can be compared with the $A_R - \varepsilon$ value determined from the height of the prewave. The usual assumption (*e.g.* ref. 54) that the latter method gives directly the value of A_R is not correct.

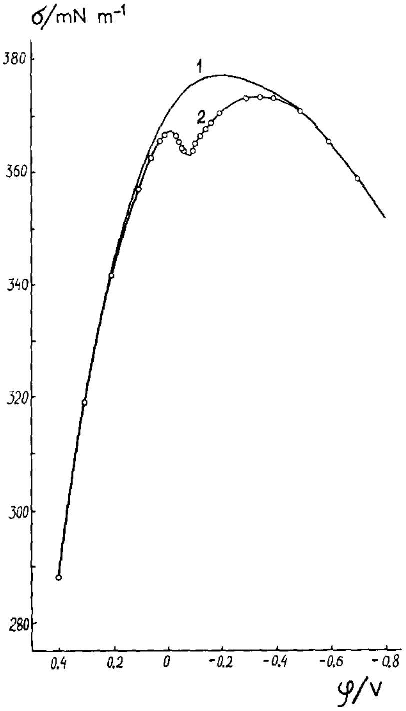

Fig. 2. Dependence of interfacial tension on potential (*vs.* aq. SCE): (1) 1 *M* H_2SO_4, (2) 0.01 *M* anthraquinone + 1 *M* H_2SO_4 in dimethylformamide[59].

redox systems by means of a capillary electrometer, *i.e.* by the same method as was used for measuring the curve of Fig. 1, was carried out by Bezugly and Korshikov[59]. These authors observed on the electrocapillary curves of acid solutions of anthraquinone and 2-iodo-anthraquinone in various solvents, two well-defined maxima and a sharp drop of σ as the potential of the beginning of anthraquinone reduction was approached. An example of the results obtained by these authors is given in Fig. 2. The similarity between the curves of Fig. 1 and 2 is obvious.

From the maximum value of $\partial\sigma/\partial\varphi$ which is observed in Fig. 2 at $\varphi \sim 0.045$ (*vs.* aqueous SCE), taking into account that $\exp(2F/RT)(\varphi-\varphi_{\frac{1}{2}}) \sim 15$ and that therefore the term A_O in eqn. (46) can be neglected, we find for the total charge $\varepsilon - A_R$ the value $\sim -12\ \mu C\ cm^{-2}$. This indicates a strong adsorption of A_R at a potential more positive than $\varphi_{\frac{1}{2}}$*. A separate determination of A_R and ε is impossible within the framework of a strictly thermodynamic treatment. Further experimental work in this direction is planned.

SUMMARY

The notion of the charge has been considered for the case of an ideally polarized

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* The given value of $A_R - \varepsilon$ is too large to be accounted for by the term $-\varepsilon$ only (non-thermodynamic conclusion!). The sharp rise of σ at potentials somewhat more negative than $\varphi_{\frac{1}{2}}$ indicates a strong adsorption of A_O. Apparently both components of the redox system are present simultaneously in the adsorbed layer.

electrode. It has been proved necessary to distinguish between the total charge, which figures in thermodynamic relations, and the free charge, which can be determined only in terms of a certain electric double-layer model. A definition of the total charge is given, equally applicable to ideally polarized and reversible electrodes, as the amount of electricity to be supplied to the electrode to keep the electrode potential constant when its surface is increased by unity and the composition of the bulk phases of the system is maintained constant. The total charge thus determined satisfies in all cases the Lippmann equation. Expressions are given for the Lippmann equation for reversible redox systems, as exemplified by platinum–hydrogen and amalgam–thallium electrodes. It has been shown that in such systems two kinds of electrocapillary curves can be obtained, depending on which chemical potential is held constant: that of the oxidised or that of the reduced component. The number of characteristic electrocapillary curves in the general case of a reversible redox system has been shown to be equal to that of the independent variables in the Nernst equation expressing the conditions of electrochemical equilibrium of the system. The results obtained have been used for the interpretation of the electrocapillary dependences observed under polarographic conditions.

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