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ELECTRIC DOUBLE LAYER ON PLATINUM-GROUP METALS AND THE ESIN–MARKOV EFFECT

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THERMODYNAMICAL RELATIONS

The thermodynamics of surface phenomena on platinum-group metals (Pt, Rh) electrodes was considered in refs. 1–7 where some of the thermodynamical relations derived were also confirmed by experiment. In these studies, however, use was made of the chemical potential of the H^+ ion, μ_{H^+}, *i.e.*, of a quantity that cannot be determined from experimental data in the general case. This partly limits the applicability of the results to dilute solutions. In the present communication we want, primarily, to eliminate this limitation.

Let us consider a solution containing a neutral salt, CA, and an acid, HA. Let μ_{HA} and μ_{CA} be the chemical potentials of HA and CA, Γ_{HA} and Γ_{CA} the surface densities of these components which are understood to mean the amounts of HA and CA to be introduced into the system for the solution composition to remain unchanged with an increase in the interface by 1 cm^2 ($\Gamma_{H_2O}=0$), μ_H and Γ_H the chemical potential and surface density of hydrogen, respectively, φ_r the electrode potential measured against the hydrogen electrode in the same solution in equilibrium with H_2 at atmospheric pressure and σ the surface density of free energy. As in refs. 3–5, Γ and μ are expressed in electrical units.

It is evident that

$$\Gamma_{HA}=\Gamma_{H^+};\quad \Gamma_{CA}=\Gamma_{C^+};\quad \Gamma_{A^-}=\Gamma_{HA}+\Gamma_{CA};\quad \Gamma_{H^+}=\Gamma_{A^-}-\Gamma_{C^+} \tag{1}$$

Subsequent conclusions are based on the equation

$$d\sigma=-\Gamma_H d\mu_H-\Gamma_{HA}d\mu_{HA}-\Gamma_{CA}d\mu_{CA} \tag{2}$$

derived from Gibbs thermodynamics or, since

$$d\mu_H=-d\varphi_r \tag{3}$$

$$d\sigma=\Gamma_H d\varphi_r-\Gamma_{HA}d\mu_{HA}-\Gamma_{CA}d\mu_{CA} \tag{4}$$

It follows from eqn. (4) that

$$\left(\frac{\partial \Gamma_H}{\partial \mu_{HA}}\right)_{\varphi_r,\mu_{CA}} = -\left(\frac{\partial \Gamma_H}{\partial \varphi_r}\right)_{\mu_{HA},\mu_{CA}} \left(\frac{\partial \varphi_r}{\partial \mu_{HA}}\right)_{\Gamma_H,\mu_{CA}} = -\left(\frac{\partial \Gamma_{HA}}{\partial \varphi_r}\right)_{\mu_{HA},\mu_{CA}} \quad (5)$$

$$\left(\frac{\partial \varphi_r}{\partial \mu_{HA}}\right)_{\Gamma_H,\mu_{CA}} = \left(\frac{\partial \Gamma_{HA}}{\partial \varphi_r}\right)_{\mu_{HA},\mu_{CA}} : \left(\frac{\partial \Gamma_H}{\partial \varphi_r}\right)_{\mu_{HA},\mu_{CA}} =$$

$$= \left(\frac{\partial \Gamma_{H^+}}{\partial \varphi_r}\right)_{\mu_{HA},\mu_{CA}} : \left(\frac{\partial \Gamma_H}{\partial \varphi_r}\right)_{\mu_{HA},\mu_{CA}} \quad (6)$$

As was shown in refs. 3–5, the change in Γ_H is related to the quantity of electricity, Q, imparted to the electrode from outside by the equation

$$\Delta \Gamma_H = -\Delta Q \quad (7)$$

provided the electrode is not accessible to any substances which, in the potential range under consideration, can act as oxidizing or reducing agents, and molecular H_2 is not evolved in the bulk of the solution in measurable quantities. Thus, eqn. (6) can be written as:

$$\left(\frac{\partial \varphi_r}{\partial \mu_{HA}}\right)_{Q,\mu_{CA}} = -\left(\frac{\partial \Gamma_{HA}}{\partial \varphi_r}\right)_{\mu_{HA},\mu_{CA}} : \left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu_{HA},\mu_{CA}}$$

$$= -\left(\frac{\partial \Gamma_{H^+}}{\partial \varphi_r}\right)_{\mu_{HA},\mu_{CA}} : \left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu_{HA},\mu_{CA}} \quad (8)$$

For the practical use of eqn. (8) it is important that the effect of dissolved H_2 upon μ_{HA} and μ_{CA} can be neglected. Therefore, with HA and CA constant, and φ_r (and hence, μ_H) changing, μ_{HA} and μ_{CA} remain constant.

Two particular cases of eqn. (8) are of especial interest.

1. Pure acid solution, [CA]=0.

In this case eqn. (8) is simplified

$$\left(\frac{\partial \varphi_r}{\partial \mu^{\pm}_{HA}}\right)_Q = -2\left(\frac{\partial \Gamma_{H^+}}{\partial \varphi_r}\right)_{\mu^{\pm}_{HA}} : \left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu^{\pm}_{HA}} \quad (9)$$

where $\mu^{\pm}_{HA}$ is the mean chemical potential of HA ions.

2. Acidified neutral salt solution in which [CA] $\gg$ [HA]. In this case, μ_{A^-} remains practically constant with changing [HA], if [CA] is constant, and, hence

$$d\mu_{HA} = d\mu_{H^+} + d\mu_{A^-} = d\mu_{H^+}$$

where $d\mu_{H^+}$ can be determined from the change in the hydrogen electrode potential with [CA] remaining constant. Under these conditions, the introduction of the quantity, μ_{H^+}, is justified. In this case, it follows from eqn. (8) that

$$\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{Q,\mu_{CA}} = -\left(\frac{\partial \Gamma_{H^+}}{\partial \varphi_r}\right)_{\mu_{H^+},\mu_{CA}} : \left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu_{H^+},\mu_{CA}} \quad (10)$$

Equations (9) and (10) express the same relations as those derived earlier. It is easy to show that eqn. (10) holds also in the case of an acid with a bivalent anion, H_2A.

The situation is somewhat more complicated in the case of changing concentration of CA with [HA] constant (see Appendix).

In some cases it is more convenient to refer the potential being measured to a constant reference electrode the potential of which does not change with μ_{HA}, rather than to a hydrogen electrode in the same solution. Let us denote the potential measured against such an electrode, by φ. If the condition [CA] $\gg$ [HA] is fulfilled and μ_{CA} is constant, it is evident that

$$d\varphi = d\varphi_r + d\mu_{H^+} \tag{11}$$

It follows from eqns. (10) and (11) that

$$\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{Q,\mu_{CA}} = 1 - \left(\frac{\partial\Gamma_{H^+}}{\partial\varphi}\right)_{\mu_{H^+},\mu_{CA}} : \left(\frac{\partial Q}{\partial\varphi}\right)_{\mu_{H^+},\mu_{CA}} \tag{12}$$

In solutions with varying concentration of HA, if the latter exceeds the applicability limits of the laws of dilute solutions, the reference of the measured potential to an electrode of constant potential is a problem lying beyond the scope of a thermodynamical treatment. However, as was shown in ref. 8, when the potential is referred to an imaginary reference electrode the potential of which differs from that of an electrode reversible with respect to the cation (in our case with respect to the H^+ ion) by the quantity $-\mu^{\pm}_{HA}$, the thermodynamical relations of electrocapillarity theory in concentrated solutions are of the same form as in dilute solutions. Therefore, such an electrode can be conditionally regarded as a constant reference electrode; in dilute solutions this definition becomes identical with the generally accepted one. Thus, for pure acid solutions with varying concentration we shall assume

$$d\varphi = d\varphi_r + d\mu^{\pm}_{HA} \tag{13}$$

It follows from eqns. (13) and (10) that

$$\left(\frac{\partial\varphi}{\partial\mu^{\pm}_{HA}}\right)_{Q} = 1 - 2\left(\frac{\partial\Gamma_{H^+}}{\partial\varphi}\right)_{\mu^{\pm}_{HA}} : \left(\frac{\partial Q}{\partial\varphi}\right)_{\mu^{\pm}_{HA}} \tag{14}$$

It was shown in refs. 4–7 how the dependence of Γ_{H^+} upon φ_r could be determined from the experimentally-obtained values of the dependence of the potential upon the solution acidity at constant Q and from the slope of the charging curve, $\partial\varphi_r/\partial Q$, and then compared with the experimental Γ_{H^+}–φ_r-curve. In refs. 3–6 the prerequisites for an experimental realization of the isoelectricity condition, *i.e.*, Q = constant, were also considered.

In the case when [CA] $\gg$ [HA], the H^+ cations can be assumed to be completely displaced from the ionic side of the double layer by the C^+ cations. Under these conditions, Γ_{H^+} can be equated with the electrode charge density, ε. In this case,

as was explained in refs. 4–5, it is assumed that the charge of the C^+ and A^- ions belongs to the ionic side of the double layer and the possibility of its being partly redistributed between the adsorbed particle and the metal is not taken into consideration, whether this corresponds to the real structure of the double layer or not. Under these assumptions, it follows from eqn. (10) that

$$\left(\frac{\partial\varepsilon}{\partial\varphi_r}\right)_{\mu_{H^+},\mu_{CA}} = -\left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{Q,\mu_{CA}}\left(\frac{\partial Q}{\partial\varphi_r}\right)_{\mu_{H^+},\mu_{CA}} \tag{15}$$

The quantity in the left-hand side of eqn. (15) is the equilibrium value of the differential capacity of the double layer at the electrode–solution interface. In principle, it would be possible to obtain this value by differentiation of the experimental Γ_{H^+}–φ_r-curve. This is, however, impracticable owing to the insufficiently accurate determination of Γ_{H^+}. Another possible method for determining the value of $\partial\varepsilon/\partial\varphi_r$ is to make a.c. measurements of the electrode differential capacity at high enough frequencies, at which the pseudocapacity of the reaction

$$H^+ + \bar{e} \rightleftarrows H_{ads.}$$

can be neglected. Apart from the experimental difficulties encountered in this case (compare for example, ref. 4), one cannot be certain that the value of $\partial\varepsilon/\partial\varphi_r$ thus found is the equilibrium value of the differential capacity of the double layer, owing to the slowness of the processes leading to the establishment of equilibrium in the ion adsorption on the surface of the platinum-group metals[4]. Thus, at the present time, the use of eqn. (15) seems to be the only possible method of determining the equilibrium value of the differential capacity of the double layer for this kind of electrode.

In solutions without an excess of the foreign cation C^+, Γ_{H^+} cannot be equated with ε since some of the H^+ ions, the surface density of which we shall denote by $\Gamma^i_{H^+}$, can take part in the formation of the ionic side of the double layer. It is evident that

$$\Gamma_{H^+} = \varepsilon + \Gamma^i_{H^+} \tag{16}$$

It follows from eqns. (9) and (16) that

$$\left(\frac{\partial\varphi_r}{\partial\mu^{\pm}_{HA}}\right)_Q = -2\left(\frac{\partial(\varepsilon+\Gamma^i_{H^+})}{\partial\varphi_r}\right)_{\mu^{\pm}_{HA}} : \left(\frac{\partial Q}{\partial\varphi_r}\right)_{\mu^{\pm}_{HA}} \tag{17}$$

and from the thermodynamical theory of electrocapillarity[8] that at small surface charges, *i.e.*, near the point of zero charge (p.z.c.), in the absence of specific adsorption, the excess amounts of cation and anion on the surface, which are opposite in sign, are equal in their absolute value to half the charge density. Assuming that this conclusion can be extended to the case under consideration, we obtain

$$\Gamma^i_{H^+} = -\Gamma_{A^-} = -\tfrac{1}{2}\varepsilon \tag{18}$$

It follows from eqns. (17) and (18) that

$$\left(\frac{\partial\varepsilon}{\partial\varphi_r}\right)_{\mu^{\pm}_{HA}} = -\left(\frac{\partial\varphi_r}{\partial\mu^{\pm}_{HA}}\right)_{Q}\left(\frac{\partial Q}{\partial\varphi_r}\right)_{\mu^{\pm}_{HA}} \tag{19}$$

It is evident from a comparison of eqns. (19) and (15) that, near the p.z.c., the same potential change with changing acidity under isoelectric conditions can be expected to occur in pure acid solutions as in the presence of an excess of neutral salt.

A relation can be readily derived from eqn. (17), that enables the Esin–Markov coefficient to be determined for platinum-group electrodes. Let us substitute Γ_H, as in refs. 1 and 2, by $A_H-\varepsilon$, where A_H is the amount of atomic hydrogen adsorbed on 1 cm^2 of surface, expressed in electrical units. Thus, taking into consideration that in an acid solution

$$\varepsilon=\Gamma_{A^-}-\Gamma^{i}_{H^+} \tag{20}$$

we find

$$dQ=-d\Gamma_H=d\varepsilon-dA_H=d\Gamma_{A^-}-d\Gamma^{i}_{H^+}-dA_H \tag{21}$$

It follows from eqns. (13), (17), (20) and (21) that

$$\left(\frac{\partial\varphi}{\partial\mu^{\pm}_{HA}}\right)_{Q} = 1+2\left(\frac{\partial\Gamma_{A^-}}{\partial\varphi}\right)_{\mu^{\pm}_{HA}}:\left[\frac{\partial(A_H-\Gamma_{A^-}+\Gamma^{i}_{H^+})}{\partial\varphi}\right]_{\mu^{\pm}_{HA}}$$

$$= \left[\frac{\partial(A_H+\Gamma_{A^-}+\Gamma^{i}_{H^+})}{\partial(A_H-\Gamma_{A^-}+\Gamma^{i}_{H^+})}\right]_{\mu^{\pm}_{HA}} \tag{22}$$

At $A_H=0$, the condition $Q=$constant becomes $\varepsilon=$constant and eqn. (22) can be presented in the form

$$\left(\frac{\partial\varphi}{\partial\mu^{\pm}_{HA}}\right)_{\varepsilon} = -\left(\frac{\partial\Gamma^{i}_{H^+}}{\partial\varepsilon}\right)_{\mu^{\pm}_{HA}}-\left(\frac{\partial\Gamma_{A^-}}{\partial\varepsilon}\right)_{\mu^{\pm}_{HA}} \tag{23}$$

Equation (23) coincides with the thermodynamical expression for the Esin–Markov effect known from electrocapillarity theory[8,10]. In contrast to mercury, however, it is inapplicable at $\varepsilon=0$, since the condition $A_H=0$ is realized only in solutions of halogen acids within a certain range of positive values of φ_r[1,5–7].

The above treatment can be readily extended to alkaline solutions, COH, and alkaline solutions of a neutral salt, CA + COH (assuming as above [CA] $\gg$ [COH] and [CA] $\approx$ constant, which justifies the introduction of the quantity μ_{OH^-}). It is evident that in alkaline solutions

$$\Gamma_{COH}=\Gamma_{OH^-};\quad \Gamma_{C^+}=\Gamma_{CA}+\Gamma_{COH};\quad \Gamma_{A^-}=\Gamma_{CA};\quad \Gamma_{OH^-}=\Gamma_{C^+}-\Gamma_{A^-} \tag{24}$$

The stoichiometry of the charging of a hydrogen electrode in alkaline solution is expressed by the reaction

$$H_{ads.}+OH^- \rightleftarrows H_2O+\bar{e}$$

Therefore, in the presence of an excess of neutral salt

$$\varepsilon = -\Gamma_{OH^-} \tag{25}$$

and in a pure alkali solution

$$\varepsilon = -\Gamma_{OH^-} + \Gamma^{i}_{OH^-} \tag{26}$$

where $\Gamma^{i}_{OH^-}$ is the surface density of OH^- ions in the ionic side of the electric double layer.

In the case of pure alkali solutions, we obtain in place of eqns. (9) and (14)

$$\left(\frac{\partial \varphi_r}{\partial \mu^{\pm}_{COH}}\right)_Q = -2\left(\frac{\partial \Gamma_{OH^-}}{\partial \varphi_r}\right)_{\mu^{\pm}_{COH}} : \left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu^{\pm}_{COH}} \tag{27}$$

$$\left(\frac{\partial \varphi}{\partial \mu^{\pm}_{COH}}\right)_Q = -1-2\left(\frac{\partial \Gamma_{OH^-}}{\partial \varphi}\right)_{\mu^{\pm}_{COH}} : \left(\frac{\partial Q}{\partial \varphi}\right)_{\mu^{\pm}_{COH}} \tag{28}$$

where $\mu^{\pm}_{COH}$ is the mean chemical potential of the C^+ and OH^- ions, and for alkaline neutral salt solutions the following two equations replace, respectively, eqns. (10) and (12)*:

$$\left(\frac{\partial \varphi_r}{\partial \mu_{OH^-}}\right)_{Q,\mu_{COH}} = -\left(\frac{\partial \Gamma_{OH^-}}{\partial \varphi_r}\right)_{\mu_{OH^-},\mu_{COH}} : \left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu_{OH^-},\mu_{CA}} \tag{29}$$

$$\left(\frac{\partial \varphi}{\partial \mu_{OH^-}}\right)_{Q,\mu_{COH}} = -1-\left(\frac{\partial \Gamma_{OH^-}}{\partial \varphi}\right)_{\mu_{OH^-},\mu_{COH}} : \left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu_{OH^-},\mu_{COH}} \tag{30}$$

The potential, φ, in alkaline solutions is referred to a reference electrode, that differs from an electrode in the solution under consideration reversible with respect to H_2 at atmospheric pressure, by the quantity μ_{OH^-} in the case of alkaline solutions of neutral salts, and by the quantity $\mu^{\pm}_{COH}$ in the case of pure alkali.

Finally, let us attempt to extend the above relations to the potentials at which adsorbed hydrogen on the electrode surface is substituted by adsorbed oxygen, *i.e.*, to the oxygen part of the charging curve. Assuming that under these conditions the system can still be treated as reversible (to what extent this is admissible will be shown in the experimental part of the present paper), eqns. (2), (3) and (7) should be substituted by the following equations:

$$d\mu_O = d\varphi_r \tag{31}$$

$$d\sigma = -\Gamma_O d\mu_O - \Gamma_{HA} d\mu_{HA} - \Gamma_{CA} d\mu_{CA} \tag{32}$$

$$\Delta\Gamma_O = \Delta Q \tag{33}$$

where μ_O and Γ_O are also expressed in electrical units. Since the changes of sign

* It is obvious that eqns. (10) and (12) can be used in the case of alkaline neutral salt solutions instead of eqns. (29) and (30) as well.

before $d\varphi_r$ in eqn. (31) compared to eqn. (3), and before ΔQ in eqn. (33) compared to eqn. (7), are mutually compensating, eqn. (8), and all the relations derived from it, remain valid. This holds also for eqns. (27)–(30) derived for alkaline solutions. Thus, if the assumption of reversibility of the ionization reaction of adsorbed oxygen is at least approximately justified, the experimental results can be treated alike whether there is adsorbed hydrogen or oxygen present on the electrode surface. This is already apparent for the reason that, taking into account the condition $\Gamma_{H_2O}=0$, oxygen adsorption can be considered as a negative hydrogen adsorption. The case when $H_{ads.}$ and $O_{ads.}$ are present simultaneously does not require special consideration, since their presence in equivalent quantities is indistinguishable thermodynamically from water chemisorption and, according to the condition $\Gamma_{H_2O}=0$, should not be taken into account. Only that fraction of Γ_O that exceeds the equivalent of Γ_H and *vice versa* is to be taken into consideration in the calculations.

EXPERIMENTAL RESULTS

Equation (14) has been experimentally verified for a 10^{-2} *N* HCl solution on a Pt/Pt electrode (the characteristics of the electrodes used and the experimental details are given in ref. 11. In Fig. 1, the dependence of $(\partial\varphi/\partial\mu^{\pm}_{HA})_Q$ upon φ_r for a 10^{-2} *N* HCl

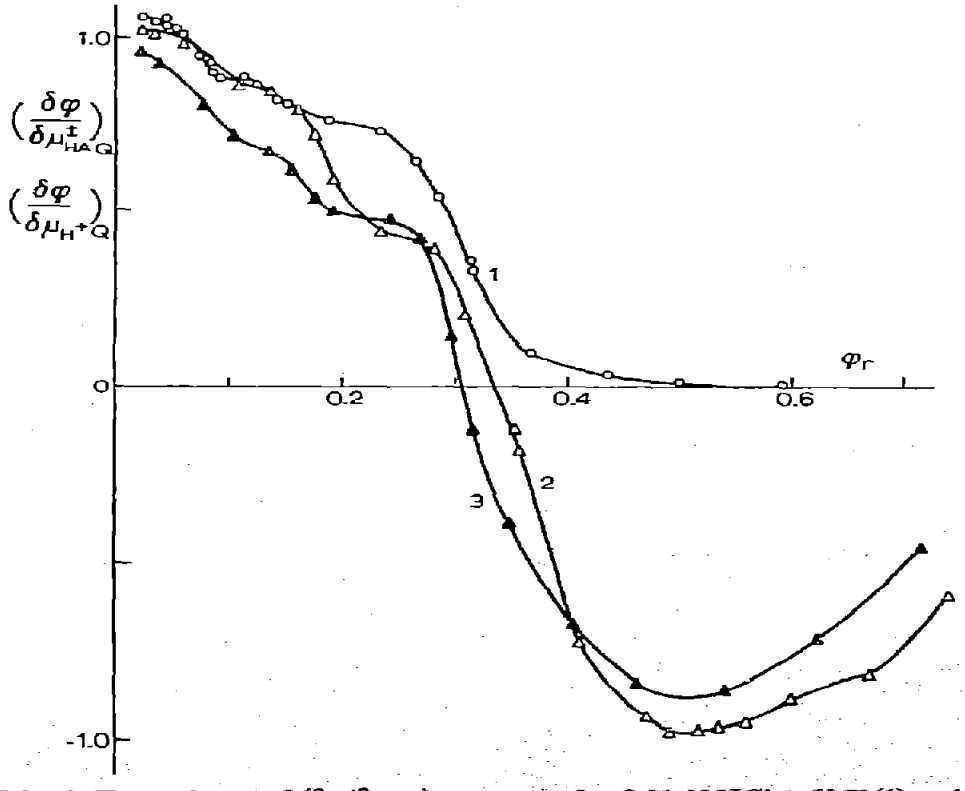

Fig. 1. Dependence of $(\partial\varphi/\partial\mu_{H^+})_Q$ upon φ_r for 0.01 *N* HCl + KCl (1) and of $(\partial\varphi/\partial\mu^{\pm}_{HA})$ upon φ_r for 0.01 *N* HCl (2) and 0.1 *N* HCl (3) on a Pt/Pt electrode.

solution (Curve 2) is compared with a similar dependence of $(\partial\varphi/\partial\mu_{H^+})_Q$ for a 10^{-2} N HCl + N KCl solution (Curve 1), which was determined previously[5,6]. The transition from experimental values of $(\partial\varphi_r/\partial\mu^{\pm}_{HA})_Q$ to $(\partial\varphi/\partial\mu^{\pm}_{HA})_Q$ was made on the basis of eqn. (13). At small φ_r the values of the derivatives for both solutions are close to unity. The reasons for this have already been discussed[5,6]. In the range of φ_r, 0.06–0.16 V, curves 1 and 2 practically coincide. Since the p.z.c. of a Pt/Pt electrode in a 10^{-2} N HCl + N KCl lies at $\varphi_r = 0.16$ V[1,5,6], the potentials, 0.06–0.16 V correspond to small negative surface charges. Therefore, the coincidence between the values of $(\partial\varphi/\partial\mu^{\pm}_{HA})_Q$ in pure acid solutions and of $(\partial\varphi/\partial\mu_{H^+})_Q$ in those with neutral salt addition appears to be due to the approximate validity of eqn. (18) for the case under consideration.

With increasing anodic potential, the values of the derivatives decrease for both solutions, but according to different laws. At $\varphi_r \gtrsim 0.5$ V in the case of a 10^{-2} N HCl + N KCl solution, $(\partial\varphi/\partial\mu_{H^+})_Q$ vanishes which, as was shown earlier, is the result of the disappearance of A_H. In a pure acid solution, in the range of values of φ_r at which $A_H = 0$, $(\partial\varphi/\partial\mu^{\pm}_{HA})_Q$ passes through a minimum, reaching a value close to -1. Thus, in the above range of φ_r, in an acid solution without a neutral salt addition, the Pt/Pt electrode under isoelectric conditions behaves approximately as a reversible chlorine electrode.

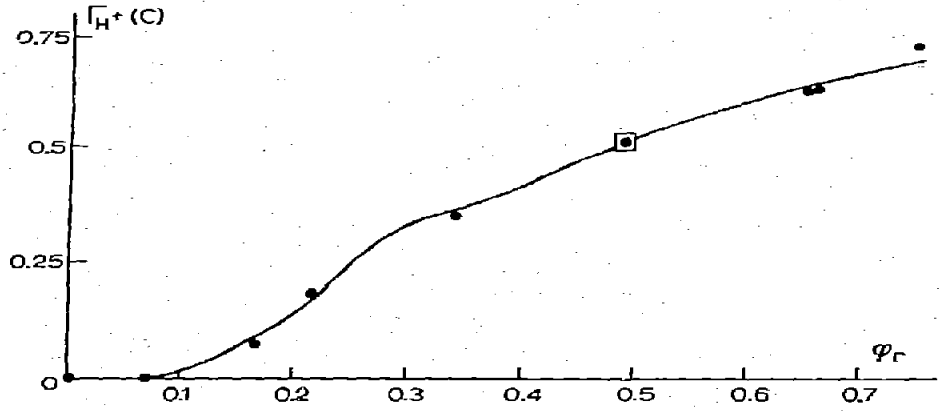

Fig. 2. Comparison of: (—), theoretically calcd. (by means of eqn. (9)) and (●), exptl. dependences of Γ_{H^+} upon φ_r for 0.01 N HCl on a Pt/Pt electrode. Γ_{H^+} is given in coulombs for the whole electrode surface. (⊡), Γ_{H^+}-value used in the determination of the integration constant.

In Fig. 2, the $\Gamma_{H^+}\varphi_r$-curve calculated from eqn. (9) is compared with the experimental curve. In Fig. 2 and in Figs. 5 and 6, the experimental values of Γ_{H^+}, which were used in the determination of the integration constant, are marked with a special symbol. A quantitative agreement between the theoretically-calculated curve and the experimental curve is observed over the whole potential range investigated.

Equations (10) and (29) were verified for the following systems: N KCl + 0.01 N HCl[7], N Na_2SO_4 + 0.01N H_2SO_4 and N KCl + 0.01 N KOH[12] on Pt coated with Rh black, and N KCl + 0.01 N HCl on Pt coated with Ru black[13]. The preparation of the electrodes and experimental details have already been described[7,12,13].

In Figs. 3 and 4 are shown the experimentally-determined dependences of $(\partial\varphi/\partial\mu_{H^+})_Q$ upon φ_r for the systems investigated.

As is evident from Fig. 3, the dependence of $(\partial\varphi/\partial\mu_{H^+})_Q$ upon φ_r for the Rh electrode in an acidified KCl solution has, on the whole, the same shape as the similar dependence for the Pt/Pt electrode. At small φ_r, the Rh electrode behaves as a reversible hydrogen electrode in equilibrium with hydrogen gas at constant pressure. At $\varphi_r \gtrsim 0.4$ V, $(\partial\varphi/\partial\mu_{H^+})_Q = 0$, from which it can be inferred that on a Rh electrode in acidified chloride solutions, A_H becomes zero. In contrast, in acidified sulfate and

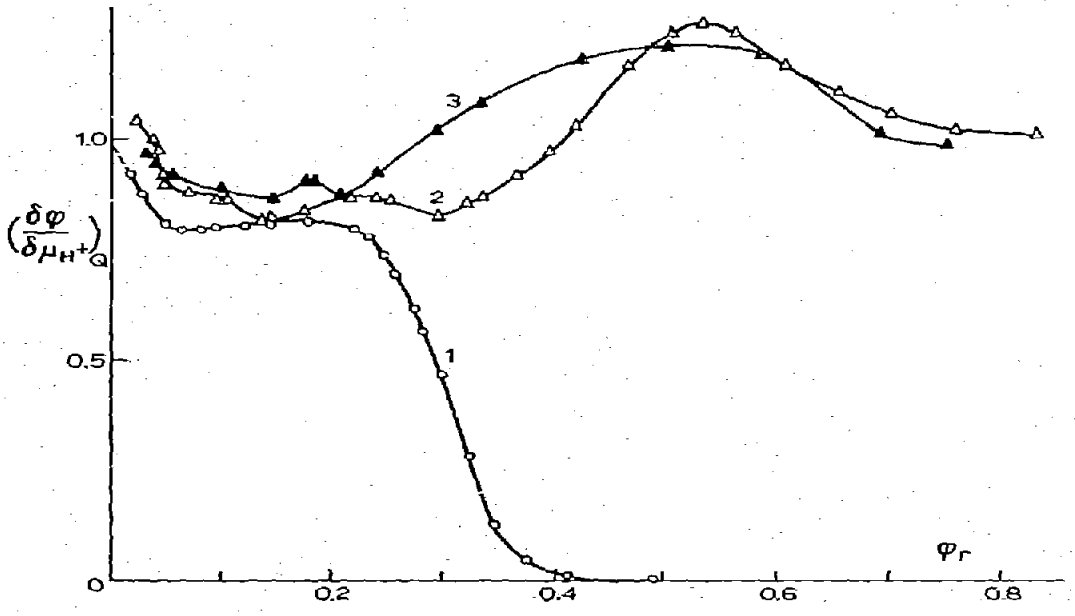

Fig. 3. Dependence of $(\partial\varphi/\partial\mu_{H^+})_Q$ upon φ_r for: (1), 0.01 N HCl + N KCl; (2), 0.01 N H_2SO_4 + N Na_2SO_4; (3), 0.01 N KOH + N KCl on Rh black electrode.

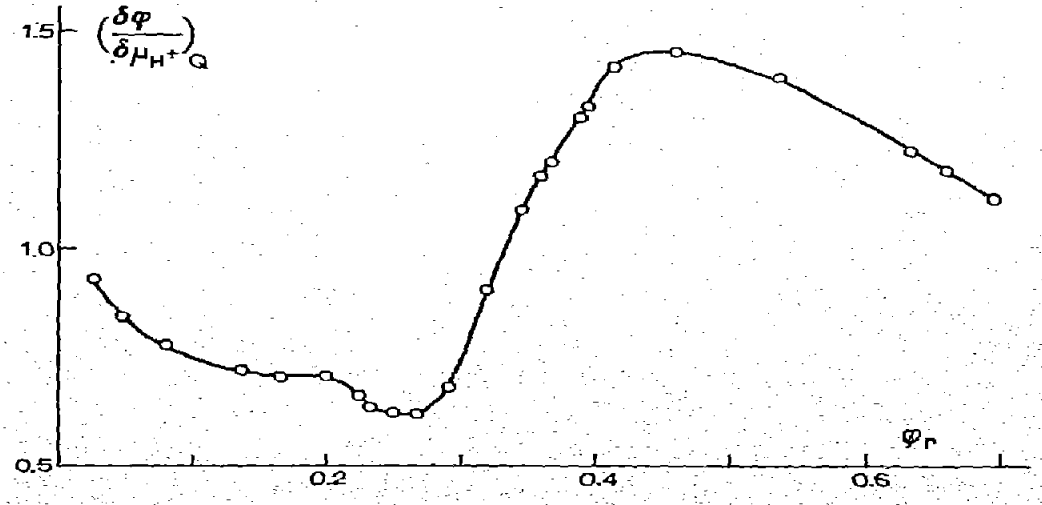

Fig. 4. Dependence of $(\partial\varphi/\partial\mu_{H^+})_Q$ upon φ_r for 0.01 N HCl + N KCl on a Ru black electrode.

alkaline chloride solutions in the potential range 0–0.8 V, the value of $(\partial\varphi/\partial\mu_{H^+})_Q$ remains close to unity. This phenomenon can be accounted for only by the absence in such solutions of a potential range in which $A_H=0$ owing to the overlapping of the hydrogen and oxygen adsorption regions. On the Ru electrode a similar situation obtains in acidified chloride solutions. Thus, on Ru, even at high concentrations of Cl^- ions, there is a continuous transition from the hydrogen adsorption region to that of oxygen adsorption.

At $\varphi_r>0.4$ V in acidified sulfate solutions and at $\varphi_r>0.3$ V in alkaline chloride solutions on Rh, and at $\varphi_r>0.35$ V in an acidified chloride solution on Ru, $(\partial\varphi/\partial\mu_{H^+})_Q$

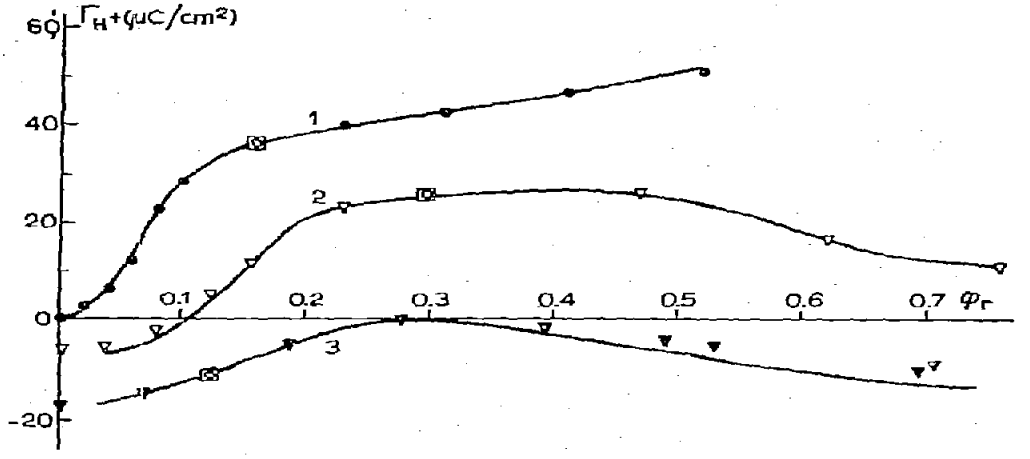

Fig. 5. Comparison of the calcd. (by means of eqn. (10)) (full drawn curve) and exptl. (dots) dependences of Γ_{H^+} upon φ_r for: (1), 0.01 N HCl + N KCl; (2), 0.01 N H_2SO_4 + N Na_2SO_4; (3), 0.01 N KOH + N KCl on a Rh black electrode.

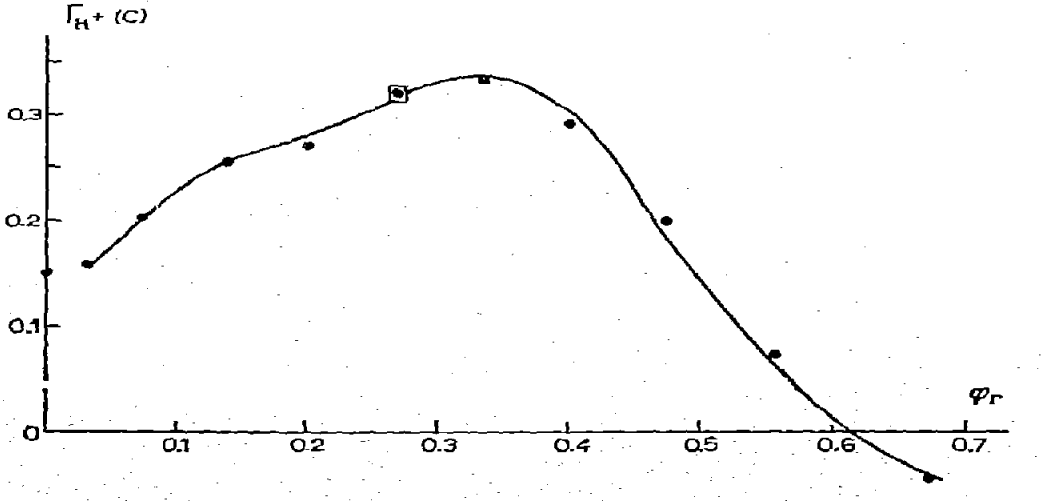

Fig. 6. Comparison of: (—), calcd. (by means of eqn. (10)) and (●), exptl. dependences of Γ_{H^+} upon φ_r for 0.01 N HCl + N KCl on a Ru black electrode. Γ_{H^+} is given in coulombs for the whole electrode surface.

is greater than unity. According to eqn. (12), this is possible owing to the value of $\partial\Gamma_{H^+}/\partial\varphi_r$ becoming negative, *i.e.*, the dependence of Γ_{H^+} upon φ_r must pass through a maximum.

In Figs. 5 and 6, the $\Gamma_{H^+}-\varphi_r$-curves theoretically-calculated from eqn. (10) are compared with the experimental curves*. The following should be noted. In the measurements of the slow charging curves of Rh and Ru by the usual method at the potentials of hydrogen adsorption (up to ~0.3 V) the anodic and cathodic charging curves coincide. However, when the measurements are performed up to 0.8 V, an appreciable hysteresis is observed. This introduces an uncertainty into the determination of the values of $\partial Q/\partial\varphi_r$, which are necessary for calculations by means of eqn. (10). The hysteresis is apparently due to slow establishment of equilibrium in oxygen adsorption. Therefore, the charging curves were determined as follows. A certain charge was supplied to the electrode, whereupon the polarizing circuit was opened. After the establishment of a constant potential, the electrode was again polarized, etc. The potentials established at open circuit were plotted against the amount of electricity passed. To distinguish these charging curves from those measured by the conventional method, we shall call them equilibrium curves. At the potential of hydrogen adsorption, the anodic and cathodic equilibrium charging curves coincide; at the potentials of oxygen adsorption (up to 0.8 V) only a slight hysteresis is observed, so that the choice of the direction of potential change in the charging curve measurements has little effect upon the calculation of the $\Gamma_{H^+}-\varphi_r$-curves[12,13]. The anodic charging curve was used in the calculations presented.

It can be seen from Figs. 5 and 6, that there is a quantitative agreement between the theoretically-calculated and experimental $\Gamma_{H^+}-\varphi_r$-curves for acid solutions. On the Rh electrode in an alkaline solution, a quantitative agreement is observed only up to $\varphi_r \sim 0.3$ V, which is possibly due to the difficulties in the establishment of equilibrium in alkaline solutions at the potentials of oxygen adsorption. However, at more anodic potentials also, there is a great similarity between the calculated and experimental curves.

According to Fig. 5, the p.z.c. of a Rh electrode in N $Na_2SO_4+0.01$ N H_2SO_4 solution lies at $\varphi_r \gtrsim 0.10$ V, and in N KCl+0.01 N HCl solution, at $\varphi_r \gtrsim 0$ V, *i.e.*, $\varphi_{z.c.}$ is −0.04 and −0.12 V, respectively. The value of the p.z.c. of a Rh electrode in a sulfate solution coincides with that determined by the tracer method[15]. As was shown earlier[1,16,17] also for a Pt/Pt electrode, no p.z.c. in the usual sense is observed with a Rh electrode in alkaline solution. After passing through a minimum, the cation adsorption begins to increase again. At $\varphi_r=0$, a marked acid adsorption is observed on a Ru electrode. In other words, the p.z.c. of Ru lies at a negative potential. The abcissa axis intersects with the $\Gamma_{H^+}-\varphi_r$-curve only at $\varphi_r \sim 0.61$ V. This potential can be considered as a p.z.c. of oxidized Ru.

Figure 7 shows the differential capacity curves of a Pt/Pt and Rh black electrodes in N KCl+0.01 N HCl and N $Na_2SO_4+0.01$ N H_2SO_4 solutions, respectively.

* The values of Γ_{H^+} on the Rh electrode are given/cm² of true surface which was determined from the hydrogen section of the charging curve according to ref. 14.

The differential capacity curves were calculated from eqn. (15). The curves obtained have a feature in common, *viz.* at the potentials of hydrogen adsorption they pass through a pronounced maximum.

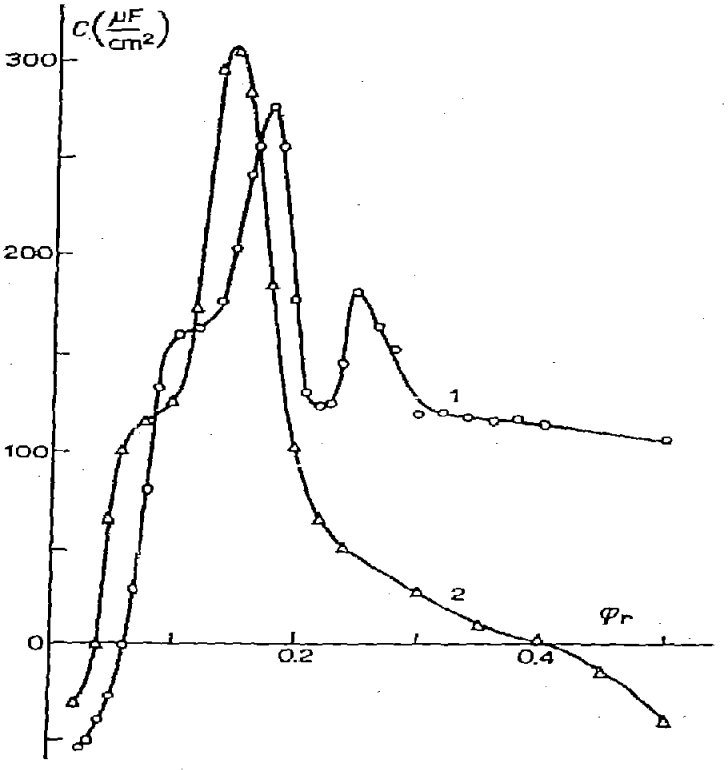

Fig. 7. Dependence of the differential capacity of the electric double layer upon φ_r on: (1), Pt/Pt electrode in 0.01 *N* HCl + *N* KCl; (2), Rh black electrode in 0.01 *N* H_2SO_4 + *N* Na_2SO_4. The capacity values are calcd./cm² of the true surface of the electrodes.

DISCUSSION OF RESULTS

The quantitative agreement between the theoretically-calculated and experimental Γ_{H^+}–φ_r-curves justifies treating the surface of the platinum-metals electrodes in solutions of varying composition as equilibrium systems, the state of which at μ_{CA} = constant is determined by the independent variables, μ_H and μ_{HA} or μ_{COH}. Especially interesting, and even somewhat surprising, is the fact that the assumption of reversibility holds not only for potentials of hydrogen adsorption, but to some extent also for those of oxygen adsorption, at least in acid solutions.

According to the Γ_{H^+}–φ_r-curves, the appearance of adsorbed oxygen on the surface of Rh and Ru electrodes brings about a decrease in anion adsorption, as was earlier observed on a Pt/Pt electrode[1,16,17]. Similar relationships appear to exist between the cation and hydrogen adsorptions*. Thus, the values of $(\partial\varphi/\partial\mu_{H^+})_Q$ on a

* A small maximum of cation adsorption had already been observed in ref. 1 in an approximate calculation of the adsorption curve.

Rh electrode in a 10^{-2} N H_2SO_4+N Na_2SO_4 solution at small φ_r are larger than unity, which should correspond to a decrease of Γ_{C^+} with decreasing φ_r. With direct adsorption measurements, however, a decrease in the cation adsorption could not be detected with certainty. Apparently, the method of measuring the dependence of the potential upon pH of the solution at constant Q (which gives directly the slope of the adsorption curve) permits a more accurate determination of the shape of the adsorption curve on approaching to $\varphi_r=0$. At low φ_r, however, it becomes difficult to realize isoelectric conditions of the experiments and definite conclusions can be drawn only when the experimental technique is further refined, in accordance with the theory set out in ref. 5, to fit the case of the presence of dissolved H_2 in the solution in measurable concentrations.

As is evident from Fig. 1, on a Pt/Pt electrode in pure acid solutions at the potentials of the double-layer region $\partial\varphi/\partial\mu^{\pm}_{HA}=-1$. In other words, the electrode potential, φ, shifts by ~ 58 V when the HCl concentration is changed by one order of magnitude. Thus, the Esin–Markov effect associated with the discrete structure of the double layer is not observed with a Pt electrode in the case of Cl^- ions. In this respect, the Pt electrode differs from the Hg electrode. The absence of the effect of discreteness may be assumed to be due to a strong chemisorptive interaction between the adsorbed anions and the platinum surface, which results in the anions sharing their charges, to a considerable degree, with the metal*. According to eqn. (40)**, the absence of any appreciable super-equivalent adsorption of cations and anions[4,17] on platinum also points to the absence of a Esin–Markov effect. The high values of the electric double-layer capacity of the Pt/Pt electrode at the potentials of the double-layer region ($\sim$70–100 μF/cm^2) are an indication of a strong deformation of anions upon adsorption. The decrease of the capacity observed in the case of Rh in $H_2SO_4+Na_2SO_4$ (Fig. 7, curve 2) is caused by the appearance of oxygen.

The differential capacity curves of the electric double layer of a Pt/Pt electrode, given in the present paper, show some interesting features. The decrease in the capacity on approaching to $\varphi_r=0$, due to the surface coverage with adsorbed hydrogen, had already been observed and discussed in the literature[1,4]. The data obtained show that a similar phenomena is also observed on a Rh electrode. The decrease in the capacity on lowering φ_r is preceded by a strong increase up to values of the order of 300 μF/cm^2 in the region of hydrogen adsorption. In the case of the Pt/Pt electrode, the highest value of the capacity is observed near the p.z.c. of the electrode. This coincidence seems to be accidental, however, since on a Rh electrode the maximum is observed at potentials that are remote from the p.z.c. Thus, the capacity maximum cannot be explained by the change in the double-layer structure with changing sign of the surface charge. Nor can the capacity maximum be associated with the peculiarities of specific anion adsorption since it is also observed in the presence of weakly adsorbable SO_4^{2-} anions. The capacity maximum seems to be due to the displacement

* According to the theory developed by LEVICH, KIRYANOV AND KRYLOV[18], the Esin–Markov effect should disappear with decreasing distance between the inner Helmholtz plane and the metal surface.
** See Appendix.

of adsorbed anions by adsorbed hydrogen, forming dipoles turned with their negative ends towards the solution and at the same time decreasing the electric double-layer capacity. A more complete interpretation of this phenomenon necessitates further investigation involving a greater number of systems.

APPENDIX

Potential change under isoelectric conditions with changing concentration of neutral salt

It follows from eqns. (4) and (7) that

$$\left(\frac{\partial \Gamma_H}{\partial \mu_{CA}}\right)_{\varphi_r,\mu_{HA}} = -\left(\frac{\partial \Gamma_{CA}}{\partial \varphi_r}\right)_{\mu_{CA},\mu_{HA}} \tag{34}$$

$$\left(\frac{\partial \varphi_r}{\partial \mu_{CA}}\right)_{\Gamma_H,\mu_{HA}} = -\left(\frac{\partial \varphi_r}{\partial \Gamma_H}\right)_{\mu_{CA},\mu_{HA}} \left(\frac{\partial \Gamma_H}{\partial \mu_{CA}}\right)_{\varphi_r,\mu_{HA}}$$

$$= -\left(\frac{\partial \Gamma_{CA}}{\partial \varphi_r}\right)_{\mu_{CA},\mu_{HA}} : \left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu_{CA},\mu_{HA}} = -\left(\frac{\partial \Gamma_{CA}}{\partial Q}\right)_{\mu_{CA},\mu_{HA}} \tag{35}$$

It follows from eqns. (35) and (1) that

$$\left(\frac{\partial \varphi_r}{\partial \mu^{\pm}_{CA}}\right)_{Q,\mu_{HA}} = -2\left(\frac{\partial \Gamma_{C^+}}{\partial Q}\right)_{\mu_{CA},\mu_{HA}} \tag{36}$$

where $\mu^{\pm}_{CA}$ is the mean chemical potential of CA ions.

Let us introduce in place of φ_r, the potential φ_{C^+} measured against an electrode reversible with respect to the C^+ cation. Since

$$\varphi_{C^+} + \mu_{C^+} = \varphi_r + \mu_{H^+} + \text{const.}$$

and, hence, $\varphi_{C^+} + \mu_{CA} = \varphi_r + \mu_{HA} + \text{const.}$, we get, according to eqn. (35)

$$\left(\frac{\partial \varphi_{C^+}}{\partial \mu_{CA}}\right)_{Q,\mu_{HA}} = -\left(\frac{\partial \Gamma_{C^+}}{\partial Q}\right)_{\mu_{CA},\mu_{HA}} - 1 \tag{37}$$

At $A_H = 0$, $dQ = d\varepsilon = d\Gamma_{A^-} - d\Gamma_{C^+}$ and eqn. (37) becomes the well known equation of electrocapillarity theory[9]:

$$\left(\frac{\partial \varphi_{C^+}}{\partial \mu_{CA}}\right)_{\varepsilon,\mu_{HA}} = -\left(\frac{\partial \Gamma_{A^-}}{\partial \varepsilon}\right)_{\mu_{CA},\mu_{HA}} \tag{38}$$

If in place of φ_{C^+}, we introduce the potential, φ, referred to an imaginary reference electrode, which is by $\mu^{\pm}_{CA}$ more negative than the electrode reversible with respect

to C^+, and which in thermodynamical relations can serve as a constant reference electrode at any concentrations[8] (see above), we obtain from eqn. (37):

$$\left(\frac{\partial\varphi}{\partial\mu^{\pm}_{CA}}\right)_{Q,\mu_{HA}} = -2\left(\frac{\partial\Gamma_{C^+}}{\partial Q}\right)_{\mu_{HA},\mu^{\pm}_{CA}} - 1 \tag{39}$$

At $A_H=0$, eqn. (39) becomes

$$\left(\frac{\partial\varphi}{\partial\mu^{\pm}_{CA}}\right)_{\varepsilon,\mu_{HA}} = -\left(\frac{\partial\Gamma_{C^+}}{\partial\varepsilon}\right)_{\mu_{HA},\mu^{\pm}_{CA}} - \left(\frac{\partial\Gamma_{A^-}}{\partial\varepsilon}\right)_{\mu_{HA},\mu^{\pm}_{CA}} \tag{40}$$

Equation (40) is a thermodynamical expression for the Esin–Markov coefficient as applied to the change in neutral salt concentration; it is similar to the relation known from electrocapillarity theory. By means of this expression, it is possible to find the coefficient in question from the $(\partial\varphi/\partial\mu^{\pm}_{CA})_{\varepsilon,\mu_{HA}}$ value at any concentrations, whereas the relation derived earlier (eqn. (9a) in ref. 5), which can be written as:

$$\left(\frac{\partial\varphi}{\partial\mu^{\pm}_{CA}}\right)_{\varepsilon,\mu_{H^+}} = -\left(\frac{\partial\Gamma_{C^+}}{\partial\varepsilon}\right)_{\mu^{\pm}_{CA},\mu_{H^+}} - \left(\frac{\partial\Gamma_{A^-}}{\partial\varepsilon}\right)_{\mu^{\pm}_{CA},\mu_{H^+}} \tag{41}$$

is applicable only to dilute solution. It can be readily shown (see footnote on p. 190) that in the case of dilute solutions, it is possible to obtain eqn. (41) from eqn. (40).

It is more convenient, for use with experimental data, to have relations expressing the dependence of φ_r or φ upon $\mu^{\pm}_{CA}$ under isoelectric conditions, not at constant μ_{HA} as for example, in eqn. (36), but at constant [HA]. This dependence can be obtained from eqn. (36) using eqns. (6) or (8), *i.e.*, by superimposing upon the change of μ_{CA} a change of μ_{HA} to bring [HA] to its original value. Assuming [CA] $\gg$ [HA], it follows from eqns. (3) and (8) that

$$\begin{aligned}\left(\frac{\partial\varphi_r}{\partial\mu^{\pm}_{CA}}\right)_{Q,[HA]} &= \left(\frac{\partial\varphi_r}{\partial\mu^{\pm}_{CA}}\right)_{Q,\mu_{HA}} + \left(\frac{\partial\varphi_r}{\partial\mu_{HA}}\right)_{Q,\mu^{\pm}_{CA}}\left(\frac{\partial\mu_{HA}}{\partial\mu^{\pm}_{CA}}\right)_{[HA]} \\ &= -2\left(\frac{\partial\Gamma_{C^+}}{\partial Q}\right)_{\mu^{\pm}_{CA},\mu_{HA}} - \left(\frac{\partial\Gamma_{H^+}}{\partial Q}\right)_{\mu^{\pm}_{CA},\mu_{HA}}\left(\frac{\partial\mu_{HA}}{\partial\mu^{\pm}_{CA}}\right)_{[HA]}\end{aligned} \tag{42}$$

It follows from eqns. (42) and (1) that

$$\left(\frac{\partial\varphi_r}{\partial\mu^{\pm}_{CA}}\right)_{Q,[HA]} =$$

$$= -\left[2 - \left(\frac{\partial\mu_{HA}}{\partial\mu^{\pm}_{CA}}\right)_{[HA]}\right]\left(\frac{\partial\Gamma_{C^+}}{\partial Q}\right)_{\mu^{\pm}_{CA},\mu_{HA}} - \left(\frac{\partial\mu_{HA}}{\partial\mu^{\pm}_{CA}}\right)_{[HA]}\left(\frac{\partial\Gamma_{A^-}}{\partial Q}\right)_{\mu^{\pm}_{CA},\mu_{HA}} \tag{43}$$

In an experimental verification of eqn. (43), $(\partial\mu_{HA}/\partial\mu^{\pm}_{CA})_{[HA]}$ can be found, for example, from the change of e.m.f. of a cell with electrodes reversible with respect to H^+ and A^- in an (HA+CA) solution on changing [CA] at constant [HA]. Since $[CA] \gg [HA]$, $\mu^{\pm}_{CA}$ can be taken from the data in the literature*.

SUMMARY

A derivation of the equations relating the potential change of an hydrogen adsorbing electrode with changing hydrogen ion activity under isoelectric conditions, to the dependence of the hydrogen ion adsorption upon the potential has been given, which can be applied to solutions of any concentration. Similar equations have been derived for alkaline solutions and for an oxygen adsorbing electrode. The calculated dependences of the hydrogen ion adsorption upon the potential have been compared with the experimental data for the following systems: Pt in 10^{-2} *N* HCl, Rh in *N* $Na_2SO_4 + 10^{-2}$ *N* H_2SO_4, Rh in *N* KCl + 10^{-2} *N* HCl, Rh in *N* KCl + 10^{-2} *N* KOH, Ru in *N* KCl + 10^{-2} *N* HCl. It has been found that in the case of Cl^- ions adsorption on Pt from HCl solutions, the Esin–Markov effect disappears; this seems to be due to the transfer of the charge of the adsorbed anions to the electrode surface. It has been shown that measurements of the dependence of the potential upon the hydrogen ion activity under isoelectric conditions in the presence of an excess of neutral salt, is a direct method for the determination of the double-layer differential capacity of a hydrogen adsorbing electrode.

REFERENCES

1 A. FRUMKIN AND A. ŠLYGIN, *Acta Physicochim. URSS*, 5 (1936) 819.
2 A. FRUMKIN, *Advan. Electrochem. Electrochem. Eng.*, Vol. 3, edited by P. Delahay, Interscience Publishers Inc., New York, 1963, p. 287.
3 A. FRUMKIN, *Elektrokhimiya*, 2 (1966) 387.
4 A. FRUMKIN, N. BALASHOVA AND V. KAZARINOV, *J. Electrochem. Soc.*, 113 (1966) 1011.
5 A. FRUMKIN, O. PETRY AND R. MARVET, *J. Electroanal. Chem.*, 12 (1966) 504.
6 O. PETRY, R. MARVET AND A. FRUMKIN, *Elektrokhimiya*, 3 (1967) 116.
7 O. PETRY, A. KOSSAYA-TSYBULEVSKAYA AND YU. TYURIN, *Elektrokhimiya*, 3 (1967) 617.
8 A. FRUMKIN, *Zh. Fiz. Khim.*, 30 (1956) 2066.
9 S. CRAXFORD, O. GAITY AND H. A. C. MCKAY, *Phil. Mag.*, 22 (1936) 359.

* In dilute solutions where the inequality $[CA] \gg [HA]$ is valid, μ_{A^-} can be equated with $\mu^{\pm}_{CA}$, and since $\mu_{HA} = \mu_{H^+} + \mu_{A^-}$

$$\left(\frac{\partial\mu_{HA}}{\partial\mu^{\pm}_{CA}}\right)_{[HA]} = 1 \qquad (44)$$

In this case, the condition [HA] = constant coincides with μ_{H^+} = constant. Thus, for dilute solutions it follows from eqns. (43) and (44) that

$$\left(\frac{\partial\varphi_r}{\partial\mu^{\pm}_{CA}}\right)_{Q,\mu_{H^+}} = \left(\frac{\partial\varphi}{\partial\mu^{\pm}_{CA}}\right)_{Q,\mu_{H^+}} = -\left(\frac{\partial\Gamma_{C^+}}{\partial Q}\right)_{\mu^{\pm}_{CA},\mu_{H^+}} - \left(\frac{\partial\Gamma_{A^-}}{\partial Q}\right)_{\mu^{\pm}_{CA},\mu_{H^+}} \qquad (45)$$

At $A_H = 0$, eqn. (45) becomes eqn. (41).

10 R. PARSONS, *Proc. IInd Congr. Surf. Activity, Electrical Phenomena, 1957*, Butterworths, London, 1957, p. 38.
11 O. PETRY AND V. TOPOLEV, *Elektrokhimiya*, in press.
12 A. FRUMKIN, O. PETRY AND A. KOSSAYA, *Elektrokhimiya*, in press.
13 O. PETRY AND V. ENTINA, *Elektrokhimiya*, in press.
14 M. TARASEVICH, K. RADYUSHKINA AND R. BURSHTEIN, *Elektrokhimiya*, 3 (1967) 455.
15 N. BALASHOVA, A. KOSSAYA AND N. GOROKHOVA, *Elektrokhimiya*, 3 (1967) 656.
16 A. SLYGIN, A. FRUMKIN AND V. MEDVEDOVSKY, *Acta Physicochim. URSS*, 4 (1936) 911.
17 N. BALASHOVA AND V. KASARINOV, *Usp. Khim.*, 34 (1965) 1721.
18 B. LEVICH, V. KIRYANOV AND V. KRYLOV, *Dokl. Akad. Nauk SSSR*, 135 (1960) 1425.