# DEPENDENCE OF THE CHARGE OF THE SURFACE OF A PLATINUM ELECTRODE ON THE POTENTIAL IN ALKALINE SOLUTIONS

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The state of the surface of a Pt/Pt electrode in solutions of $10^{-2}$ N KOH + 1 N KX, where X = $Cl^-$, $Br^-$, or $I^-$, and $10^{-2}$ N KOH was studied by the method of isoelectric shifts of the potential, varying the pH of the solution. It was concluded that the specific adsorption of anions in alkaline solutions increases in the series $Cl^- < Br < I^-$. A quantitative coincidence of calculation and experiment was obtained, which permits us to conclude that the Gibbs thermodynamics of surface phenomena is applicable to a Pt/Pt electrode in alkaline solutions. The zero charge potential in a solution of $10^{-2}$ N KOH + 1 N KBr is equal to −0.39 V, while in a solution of $10^{-2}$ N KOH + 1 N KI it is equal to −0.52 V relative to the normal hydrogen electrode. The thermodynamic function for the dependence of the point of zero charge of the electrode, adsorbing hydrogen or oxygen, upon the pH of the solution was derived and analyzed.

The structure of the electrical double layer on platinum in alkaline solutions was investigated in [1] according to the change in the composition of the solution during the formation of a double layer and in [2] by the method of radioactive tracers. In this work the state of the surface of a Pt/Pt electrode was studied by the method of isoelectric potential shifts, varying the pH of the solution [3-5].

The procedure for the measurements and preparation of the electrodes was described in [6]. The experiments were conducted at 20 ± 1°C. The isoelectric shifts of the potential were determined by replacing solutions of $10^{-3}$ N KOH + 1.009 N KX by $10^{-1}$ N KOH + 0.91 N KX, where X = Cl, Br, or I, or by replacing a solution of $10^{-3}$ N KOH by $10^{-1}$ N OKH. Usually when the solutions were replaced, the establishment of a time-invariant potential was immediately observed. Within a period of several minutes, small changes occurred only in solutions of bromides and iodides at the potentials of the "double layer" region. In the work we used special-purity solutions of alkali, which were subjected to prolonged purification on a Pt/Pt electrode with cathodic polarization. The salts were recrystallized twice from double-distilled water and calcined (KI in an atmosphere of hydrogen). The true surface of the electrode was determined from the length of the hydrogen portion of the charging curve in 1N $H_2SO_4$ [7, 8].

The thermodynamic functions of the hydrogen electrode in alkaline solutions were considered in [9] [eqs. (27) and (29)]. Since under the conditions $\Gamma_{H_2O} = 0$, $\Gamma_{OH^-} = -\Gamma_{H^+}$, the indicated functions can be transformed into Eq. (1) in the case of solutions of alkali without the background:

$$\left(\frac{\partial\varphi_r}{\partial\mu^{\pm}_{COH}}\right)_Q = 2\left(\frac{\partial\Gamma_{H^+}}{\partial\varphi_r}\right)_{\mu^{\pm}_{COH}} : \left(\frac{\partial Q}{\partial\varphi_r}\right)_{\mu^{\pm}_{COH}}, \quad (1)$$

and Eq. (2) in solutions with an excess of an indifferent electrolyte:

$$\left(\frac{\partial\varphi_r}{\partial\mu_{OH^-}}\right)_{Q,\mu_{CA}} = \left(\frac{\partial\Gamma_{H^+}}{\partial\varphi_r}\right)_{\mu_{OH^-},\mu_{CA}} : \left(\frac{\partial Q}{\partial\varphi_r}\right)_{\mu_{OH^-},\mu_{CA}} \cdots, \quad (2)$$

where $\Gamma_{OH^-}$ and $\Gamma_{H^+}$ are the Gibbs adsorptions of the $OH^-$ and $H^+$ ions; $\varphi_r$ is the potential relative to the reversible hydrogen electrode in the same solution; $\mu^{\pm}_{COH}$ is the average chemical potential of alkali ions; $\mu_{CA}$ and $\mu_{OH^-}$ are the chemical potentials of the ions of the salts and $OH^-$, respectively; Q is the charge communicated to the system. The values of $\mu$, $\Gamma$, and Q are expressed in electrical units. In the presence of an excess of an

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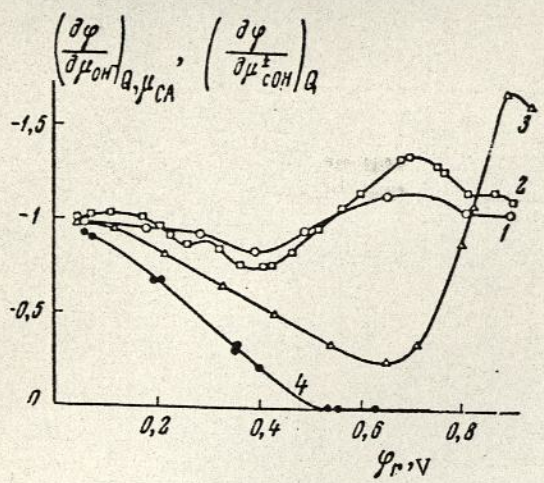


Fig. 1. Dependence of $(\frac{\partial\varphi}{\partial\mu^{\pm}_{COH}})_Q$ and $\left(\frac{\partial\varphi}{\partial\mu_{OH^-}}\right)_{Q,\mu_{CA}}$ upon $\varphi_r$ on a Pt/Pt electrode in solutions: 1) 0.01 N KOH; 2) 0.01 N KOH + 1 N KCl; 3) 0.01 N KOH + 1 N KBr; 4) 0.01 N KOH + 1 N KI.

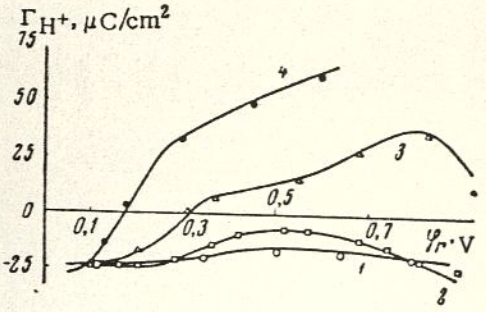


Fig. 2. Comparison of the theoretically calculated (solid lines) and experimental (points) dependence of $\Gamma_{H^+}$ upon $\varphi_r$ on a Pt/Pt electrode in solutions: 1) 0.01 N KOH; 2) 0.01 N KOH + 1 N KCl; 3) 0.01 N KOH + 1 N KBr; 4) 0.01 N KOH + 1 N KI.

indifferent electrolyte, according to the model of the double layer on platinum proposed in [3, 5], $\Gamma_{H^+}$ is equal to the charge of the metallic coating of the double layer $\varepsilon$. The values of $\partial Q/\partial\varphi$ were determined from the anodic charging curves, which were measured in the usual way, and in the investigated interval of $\varphi_r$ proved to be sufficiently reversible.

Figure 1 shows the dependence of $\left(\frac{\partial\varphi}{\partial\mu^{\pm}_{COH}}\right)_Q = \left(\frac{\partial\varphi_r}{\partial\mu^{\pm}_{COH}}\right)_Q - 1$ and $\left(\frac{\partial\varphi}{\partial\mu_{OH^-}}\right)_{Q,\mu_{CA}} = \left(\frac{\partial\varphi_r}{\partial\mu_{OH^-}}\right)_{Q,\mu_{CA}} - 1$ systems. Regardless of the composition of the solution, at low $\varphi_r$, $\left(\frac{\partial\varphi}{\partial\mu_{OH^-}}\right)_{Q,\mu_{CA}}$ and $\left(\frac{\partial\varphi}{\partial\mu^{\pm}_{COH}}\right)_Q$ are close to $-1$, i.e., the behavior of a Pt/Pt electrode approaches that in the case of equilibrium of the electrode with gaseous hydrogen at constant pressure. According to [4, 5], this means that at low $\varphi_r$, $\frac{\partial\Gamma_{H^+}}{\partial\varphi_r} \approx 0$. In the case of more anodic $\varphi_r$, a strong dependence of the shape of the curves upon the compositon of the solution is detected. Thus, in 0.01 N KOH, $\left(\frac{\partial\varphi}{\partial\mu^{\pm}_{COH}}\right)_Q$ is close to $-1$ in the entire region of $\varphi_r$, which is the result of overlapping of the regions of adsorption of hydrogen and oxygen. In the presence of KI, however, when $\varphi_r \gtrsim 0.5$ V, $\left(\frac{\partial\varphi}{\partial\mu_{OH^-}}\right)_{Q,\mu_{CA}} = 0$, i.e., at the indicated $\varphi_r$, there is no adsorbed hydrogen or oxygen on the surface of Pt in detectable amounts. From the shape of the curves obtained, it can be concluded that the specific adsorption in alkaline solutions increases in the series $Cl^- < Br^- < I^-$. This conclusion agrees with the results of measurements by other methods [7]. The interactions of the $\left(\frac{\partial\varphi}{\partial\mu^{\pm}_{COH}}\right)_Q$ or $\left(\frac{\partial\varphi}{\partial\mu_{OH^-}}\right)_{Q,\mu_{CA}}$ curves with the line

TABLE 1

| Solution | $\varphi_z$ $\varphi$ $\varphi_{zero\ charge}$, V (n.h.e.) according to [1] | according to [2] | our measurements |
|---|---|---|---|
| 1*N* NaBr + $5 \cdot 10^{-2}$*N* NaOH | −0,26 | — | — |
| 1*N* KBr + $10^{-2}$*N* KOH | — | — | −0,39 |
| $10^{-2}$*N* NaBr + $10^{-2}$*N* NaOH | — | −0,36* | — |
| $10^{-2}$*N* CsI + $10^{-2}$*N* CsOH | — | −0,55 | — |
| 1*N* KI + $10^{-2}$*N* KOH | — | — | −0,52 |

* The value of the point of zero charge in the hydrogen region is cited here. According to [2], there is also a point of zero charge in the oxygen region at 0.3 V.

corresponding to $\left(\frac{\partial\varphi}{\partial\mu_{OH^-}}\right)_{Q,\mu_{CA}}$ or $\left(\frac{\partial\varphi}{\partial\mu^{\pm}_{COH}}\right)_{Q} = -1$ characterize the positions of the extremes on the $\Gamma_{H^+}$ versus $\varphi_r$ curves [5, 9].

In Fig. 2 the calculated $\Gamma_{H^+}$ versus $\varphi_r$ curves are compared with the experimental curves, found by titrating the solution [1, 6]. A quantitative coincidence of calculation and experiment is observed for all the investigated systems. The shape of the $\Gamma_{H^+}$ versus $\varphi_r$ curves is analogous to the shape of the corresponding curves described in the literature [1, 2]. The values of $\Gamma_{H^+}$, which, according to our data, comprise ~ 22-23 $\mu C/cm^2$ at $\varphi_r$ = 0.04 V, are close to those found in [1] and somewhat higher than those obtained in [2] (~15 $\mu C/cm^2$ in $10^{-2}$ N NaOH + $10^{-2}$ N NaBr and ~20 $\mu C/cm^2$ in $10^{-2}$ N CsOH). Table 1 summarizes the zero charge potentials $\varphi_{z.c.}$ of platinum in alkaline solutions according to the data of various authors.

The results of a determination of the point of zero charge in this work, in general agree with the data of measurements using radioactive tracers.

Figure 3 shows the anodic charging curves in the investigated solutions and the curves of the dependence of the amount of hydrogen adsorbed on the electrode, $A_H$, upon $\varphi_r$, calculated according to the equation:

$$Q = \Gamma_{H^+} - A_H. \tag{3}$$

On the $A_H$ versus $\varphi_r$ curve in a solution of $10^{-2}$ N KOH ÷ 1 N KI there is a vertical portion, corresponding to $K_H = 0$. The behavior of a Pt/Pt electrode in a solution of $10^{-2}$ N KOH + 1 N KI is thus analogous to the behavior in a solution of $10^{-2}$ N HCl + 1 N KCl [5, 6]. No vertical portions are observed on the other curves, which is a result of overlapping of the regions of adsorption of hydrogen and oxygen.

The curves of the equilibrium differential electrical double-layer capacitance [9] $C = \left(\frac{\partial\varepsilon}{\partial\varphi_r}\right)_{\mu_{OH^-}\mu_{CA}}$, obtained according to Eq. (2), are given in Fig. 4. At the potentials of the double-layer region in a solution of 1 N KI + $10^{-2}$ N KOH, the capacitance is equal to ~70 $\mu F/cm^2$. When $\varphi_r$ decreases, the C versus $\varphi_r$ curve passes through a maximum at the potentials of the hydrogen region, the height of which reaches ~400 $\mu F/cm^2$. Such high values of the capacitance are due to the occurrence of a process of displacement of anions by the dipoles of adsorbed hydrogen [9, 10].

The results presented in Fig. 2 permit us to conclude that the thermodynamic theory of the hydrogen electrode [3] is applicable to the Pt/Pt electrode in alkaline solutions. Such a conclusion was obtained earlier in measurements of Pt in acid solutions [5, 6], as well as on Rh [9], Ru, and Pt + Ru alloy [9, 11].

The value of $\Gamma_{H^+}$ in alkaline solutions, found in this work, just like that obtained by other methods in [1, 2], in the absence of specifically adsorbed anions, depends little upon $\varphi_r$. Such a phenomenon is apparently explained by random compensation of two effects: the adsorption of cations, related to the ionization of $H_{abs}$ and decreasing

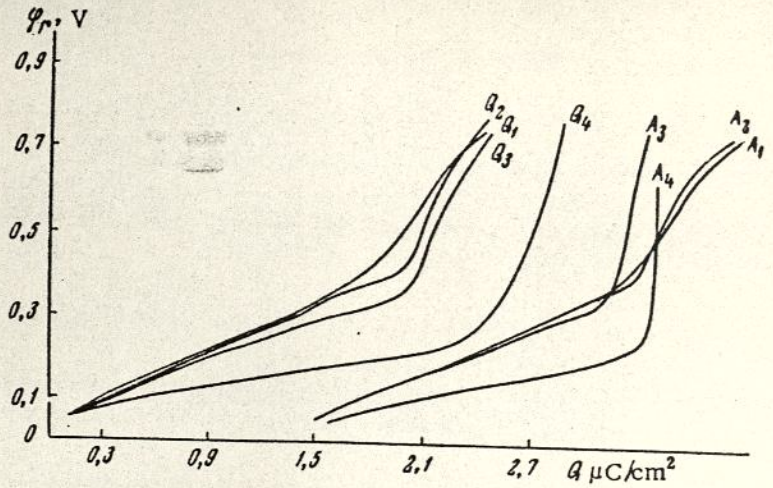


Fig. 3. Charging curves (a) and $A_H$ versus $\varphi_r$ curves (b) on a Pt/Pt electrode in solutions 1) 0.01 N KOH; 2), 0.01 N KOH + 1 N KCl; 3) 0.01 N KOH + 1 N KBr; 4) 0.01 N KOH + 1 N KI.

with increasing $\varphi_r$, and the adsorption by hydrated surface oxide groups, increasing within some interval of $\varphi_r$ [12]. This form of adsorption may be considered just like the adsorption of anions with the composition $ONa^-$ (or $O_2Ba^{2-}$ in the case of doubly charged cations [13]). The specifically adsorbed anions displace the $ONa^-$ ions from the surface, which leads to a substantial change in the shape of the $\Gamma_{H^+}$ versus $\varphi_r$ curve.

A comparison of $\varphi_{z.c.}$ in alkali bromide, cited in Table 1, with $\varphi_{z.c.}$ in a solution of $10^{-2}$ N HBr + 1 N NaBr, equal to 0.02 V [1], leads to the conclusion that $\varphi_{z.c.}$ of platinum is shifted with changing pH in the presence of $Br^-$ ions, which, according to the data of various authors, is from 0.25 to 0.35 V. As was indicated in [3, 12], the point of zero charge of metals adsorbing hydrogen and oxygen can be shifted with changing pH of the solution. Let us consider this question in greater detail. From the Gibbs equation, written as applied to the hydrogen electrode under the condition of an excess of an indifferent electrolyte [3, 4]:

$$d\sigma = \Gamma_H d\varphi_r - \Gamma_{H^+} d\mu_{H^+} \tag{4}$$

it follows that

$$\left(\frac{\partial \Gamma_H}{\partial \mu_{H^+}}\right)_{\varphi_r} = -\left(\frac{\partial \Gamma_{H^+}}{\partial \varphi_r}\right)_{\mu_{H^+}}, \tag{5}$$

$$\left(\frac{\partial \Gamma_{H^+}}{\partial \varphi_r}\right)_{\mu_{H^+}} \left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Gamma_{H^+}} \left(\frac{\partial \mu_{H^+}}{\partial \Gamma_{H^+}}\right)_{\varphi_r} = -1 \tag{6}$$

or

$$\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Gamma_{H^+}} = \left(\frac{\partial \Gamma_{H^+}}{\partial \Gamma_H}\right)_{\varphi_r}. \tag{7}$$

In the functions cited, $\varphi$ is the free surface energy per $cm^2$; $\Gamma_H$ is the Gibbs adsorption of hydrogen; $\mu_{H^+}$ is the chemical potential of $H^+$ ions. If we use the model of the structure of the double layer on Pt given in [3, 5], then Eq. (7), expresses the shift of $\varphi_r$ with the pH at a constant charge of the double layer. Considering Eq. (3), Eq. (7) can be represented in the form:

$$\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Gamma_{H^+}} = 1\Big/\left[\left(\frac{\partial A_H}{\partial \Gamma_{H^+}}\right)_{\varphi_r} - 1\right] = 1\Big/\left[\left(\frac{\partial A_H}{\partial \mu_{H^+}}\right)_{\varphi_r} : \left(\frac{\partial \Gamma_{H^+}}{\partial \mu_{H^+}}\right)_{\varphi_r} - 1\right] \tag{8}$$

or

$$\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{\Gamma_{H^+}}=\left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{\Gamma_{H^+}}+1=\left(\frac{\partial A_H}{\partial\Gamma_{H^+}}\right)_{\varphi_r}\Big/\left[\left(\frac{\partial A_H}{\partial\Gamma_{H^+}}\right)_{\varphi_r}-1\right], \qquad (8a).$$

where $\varphi$ is the potential, measured relative to the normal hydrogen electrode. An analysis of Eqs. (8) and (8a) permits us to estimate the possible values of $\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{\Gamma_{H^+}}$.

As it follows from Eqs. (8) and (8a). $\left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{\Gamma_{H^+}}=-1$ or $\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{\Gamma_{H^+}}=0$, i.e., $\varphi_{z.c.}$ does not depend on the pH, if $\left(\frac{\partial A_H}{\partial\mu_{H^+}}\right)_{\varphi_r}=0$, and in particular, when $A_H=0$. This conclusion is confirmed by measurements on metals that do not adsorb hydrogen, for example, on mercury [14]. Recently Balashova and associates did not detect any dependence of $\varphi_{z.c.}$ of Pt upon the pH in solutions of $H_2SO_4 + Na_2SO_4$ (within the interval of pH from 2 to 5) by the method of radioactive tracers. In the investigated solutions, $\varphi_{z.c.}$ of Pt is close to the region of $\varphi_r$ in which, insofar as can be judged from the data of [3], the following condition is approximately fulfilled:

$$\left(\frac{\partial A_H}{\partial\mu_{H^+}}\right)_{\varphi_r}=0.$$

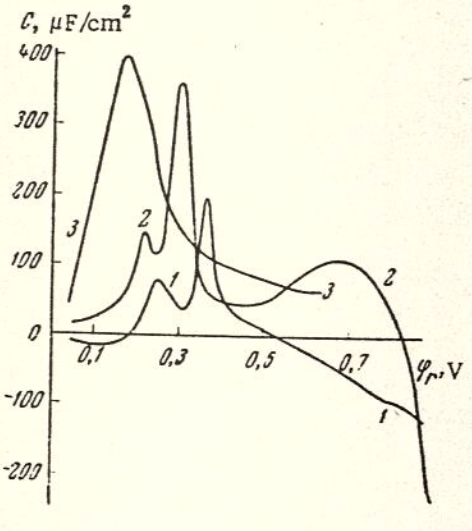


Fig. 4. Dependence of the equilibrium differential double-layer capacitance upon $\varphi_r$ on a Pt/Pt electrode in solutions: 1) 0.01 N KOH + 1 N KCl; 2) 0.01 N KOH + 1 N KBr; 3) 0.01 N KOH + 1 N KI.

On the other hand, the quantity $\left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{\Gamma_{H^+}}=0$ or $\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{\Gamma_{H^+}}=1$ could be strictly observed only in the case when $\Gamma_{H^+}$ did not vary with $A_H$, in the presence of variation of $\mu_{H^+}$ and observance of constancy of $\varphi_r$, which, however, contradicts the experimental data. Actually, as it follows from a comparison of the $A_H$ versus $\varphi_r$ and $\Gamma_{H^+}$ versus $\varphi_r$ curves, measured at various $\mu_{H^+}$ (in acid and alkaline solutions), a change in the pH of the solution has a greater effect on the value of $\Gamma_{H^+}$ than on the value of $A_H$. Bockris et al. [15] found by an impedance method that the shift of $\varphi_{z.c.}$ of Pt in solutions of $HClO_4 + NaClO_4$ and $NaClO_4 +$ NaOH corresponds to the equation $\left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{\varepsilon=0}\approx 0$. Thus, this result cannot be brought into agreement with the conclusions from the thermodynamic theory of the hydrogen electrode and the experimental data obtained by other methods, which has also been noted earlier [12].

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