

THE DEPENDENCE OF THE SURFACE CHARGE OF PLATINUM ELECTRODES ON THE POTENTIAL IN ALKALINE SOLUTIONS

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Abstract

The dependence of the hydrogen ions adsorption on the potential of the platinized platinum electrode in alkaline solutions of varying composition has been determined by two independent methods. The thermodynamic relations determining the change of the electrode potential with pH at constant surface charge have been considered.

The investigation of the electric double layer structure on platinum metals permits to elucidate the influence of adsorbed hydrogen and oxygen atoms on the structure of the electrode/solution interface.

The dependence of the surface charge ϵ of platinized platinum on the potential was determined for the first time in 1936 by SLYGIN, FRUMKIN and MEDVEDOVSKY¹⁾ by measuring the change in the acidity of the solution upon its contact with the electrode and establishment of the adsorption equilibrium. It was shown that in acid solutions without specifically adsorbed ions in the presence of considerable amounts of adsorbed oxygen the positive surface charge decreases with increasing potential while under corresponding conditions in the presence of adsorbed hydrogen, the negative charge remains practically constant. These results were explained assuming that adsorbed hydrogen and oxygen atoms forming dipoles with the metal surface participate in the setting up of the potential difference. In alkaline solutions of inactive ions to the first approximation ϵ proved to be independent of the potential, *i.e.* in this case the total change of the potential drop under anodic polarization is determined by the substitution of O_{ads} for H_{ads} . Later these dependences were confirmed by BALASHOVA and KAZARINOV by the radioactive tracers technique,²⁾ which gave also some additional data on the electric double layer

structure on platinum.

A method for the investigation of the state of platinized platinum surface was suggested in³⁾ which consisted in the determination of the electrode potential change with changing solution composition and constant amount of electricity stored in the system, *i.e.* under so-called isoelectric conditions. This method was used by OBRUCHEVA⁴⁾ for the investigation of specific ion adsorption on platinum. A very simple version of this method consisting in the determination of the potential change of an isolated electrode with changing solution pH was developed in Refs. from 5) to 8).

The present paper is concerned with the investigation of the state of the surface of the platinized platinum (Pt/Pt) electrode in alkaline solutions using the method of isoelectric potential shifts with changing pH.

The technique of measurements and preparation of electrodes is described in Ref. 8). The experiments were carried out at $20 \pm 1^\circ\text{C}$. The isoelectric potential shifts were determined for the cases of the substitution of $10^{-3}\text{ N KOH} + 1.009\text{ N KX}$ by $10^{-1}\text{ N KOH} + 0.91\text{ N KX}$ solutions, where $\text{X} = \text{Cl}^-, \text{Br}^-$ or I^- , or of 10^{-3} N KOH by 10^{-1} N KOH . Usually a constant potential was established practically immediately after the change of the solutions. Slight changes were observed during several minutes only in bromide and iodide solutions in the "double layer" region of potentials. High purity alkali solutions subjected to prolonged purification on the Pt/Pt electrode under cathodic polarization were used in the experiments. The salts were twice re-crystallized from twice distilled water and calcinated (KI in hydrogen atmosphere). The true surface of the electrodes was determined from the length of the hydrogen section of the charging curve in $1\text{ N H}_2\text{SO}_4$.^{9,10)}

The thermodynamic relations for the hydrogen electrode in alkaline solutions were considered in¹¹⁾ (equations (27) and (29)). Since at $\Gamma_{\text{H}_2\text{O}} = 0$, $\Gamma_{\text{OH}^-} = -\Gamma_{\text{H}^+}$, in the case of alkaline solutions without a supporting electrolyte these relations can be transformed into Eq. (1):

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

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

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

where Γ_{OH^-} and Γ_{H^+} are Gibbs adsorptions of OH^- and H^+ ions, φ_r – the potential against the reversible hydrogen electrode in the same solution, $\mu_{\text{COH}}^{\pm}$ – the mean chemical potential of alkali ions, μ_{CA} and μ_{OH^-} – the chemical poten-

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tials of the supporting electrolyte and of OH^- ions, respectively, Q —the charge imparted to the system. The quantities μ , Γ and Q are expressed in electric units. According to the model of the double layer on platinum suggested in Refs. 3) and 7), in the presence of an excess of indifferent electrolyte, Γ_{H^+} is equal to the charge of the metal side of the double layer ε . The values of $\frac{\partial Q}{\partial \varphi_r}$ were determined from the anodic charging curves measured by the conventional method, and in the investigated range of φ_r proved to be sufficiently reversible.

Fig. 1 shows the dependences $\left(\frac{\partial \varphi}{\partial \mu_{\text{COH}}^{\pm}}\right)_Q = \left(\frac{\partial \varphi_r}{\partial \mu_{\text{COH}}^{\pm}}\right)_Q - 1$ and $\left(\frac{\partial \varphi}{\partial \mu_{\text{OH}^-}}\right)_{Q, \mu_{\text{CA}}} = \left(\frac{\partial \varphi_r}{\partial \mu_{\text{OH}^-}}\right)_{Q, \mu_{\text{CA}}} - 1$ on φ_r for the systems investigated. Irrespective of the solution composition, at small φ_r $\left(\frac{\partial \varphi}{\partial \mu_{\text{OH}^-}}\right)_{Q, \mu_{\text{CA}}}$ and $\left(\frac{\partial \varphi}{\partial \mu_{\text{COH}}^{\pm}}\right)_Q$ are close to -1 , *i.e.* the behaviour of the Pt/Pt electrode approaches that observed in the case of equilibrium between the electrode and hydrogen gas at constant pressure. According to Refs. 5) and 7), this means that at small φ_r $\frac{\partial \Gamma_{\text{H}^+}}{\partial \varphi_r} \approx 0$. At more anodic φ_r the shape of the curves depends strongly on the solution composition. Thus

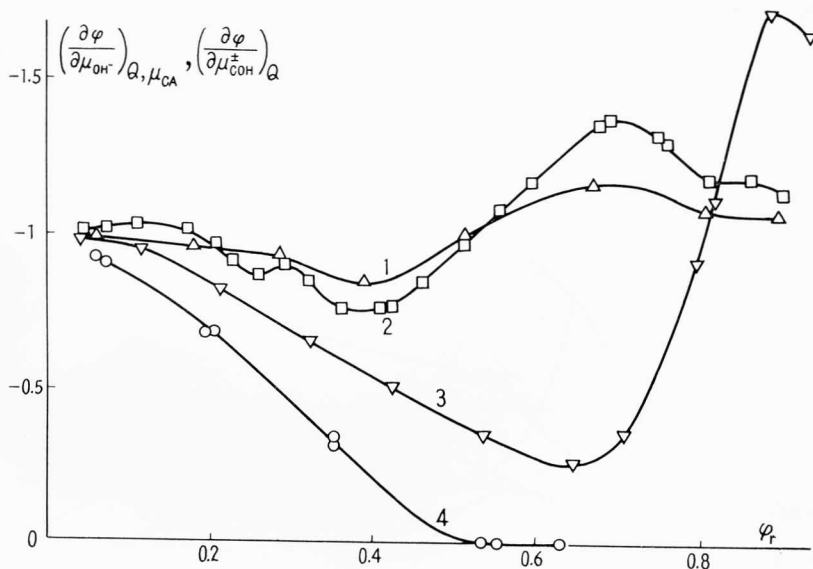


Fig. 1. Dependences of $\left(\frac{\partial \varphi}{\partial \mu_{\text{COH}}^{\pm}}\right)_Q$ and $\left(\frac{\partial \varphi}{\partial \mu_{\text{OH}^-}}\right)_{Q, \mu_{\text{CA}}}$ on φ_r on a Pt/Pt electrode in solutions: 1-0.01 N KOH, 2-0.01 N KOH+1N KCl, 3-0.01 N KOH+1N KBr, 4-0.01 N KOH+1N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

in 0.01 N KOH over the whole potential range $\left(\frac{\partial\varphi}{\partial\mu_{\text{COH}}^{\pm}}\right)_q$ is close to -1 , which is due to the overlapping of the adsorption regions of hydrogen and oxygen. In the presence of KI however at $\varphi_r \gtrsim 0.5$ V $\left(\frac{\partial\varphi}{\partial\mu_{\text{OH}^-}}\right)_{q, \text{PCA}} = 0$, *i.e.* at such φ_r values no detectable amounts of adsorbed hydrogen and oxygen are present on the platinum surface. From the shape of the obtained curves it can be concluded that specific adsorption of anions increases in the series: $\text{Cl}^- < \text{Br}^- < \text{I}^-$. This conclusion is in agreement with the results of measurements by other methods.⁹⁾ The intersections of the $\left(\frac{\partial\varphi}{\partial\mu_{\text{COH}}^{\pm}}\right)_q$ or $\left(\frac{\partial\varphi}{\partial\mu_{\text{OH}^-}}\right)_{q, \text{PCA}}$ curves with the line corresponding to $\left(\frac{\partial\varphi}{\partial\mu_{\text{COH}}^{\pm}}\right)_q = -1$ or $\left(\frac{\partial\varphi}{\partial\mu_{\text{OH}^-}}\right)_{q, \text{PCA}} = -1$ characterize the positions of the extrema on the Γ_{H^+} , φ_r -curves.^{7,11)}

In Fig. 2 the calculated Γ_{H^+} , φ_r -curves are compared with the experimental ones found by titration of the solution.^{1),8)} A quantitative agreement between calculated and experimental data is observed for all the systems investigated. The shape of the obtained Γ_{H^+} , φ_r curves is similar to that of respective curves described in the Refs. 1), 2), and 12). The values of Γ_{H^+} , which according to our data are 22–23 $\mu\text{coul}/\text{cm}^2$ at $\varphi_r = 0.04$ V, are close to those found in¹⁾ and somewhat higher than those obtained in Refs. 2) and 12) ($\sim 15 \mu\text{coul}/\text{cm}^2$ in 10^{-2} N NaBr and $\sim 20 \mu\text{coul}/\text{cm}^2$ in 10^{-2} N CsOH). Table 1 lists the potentials of zero

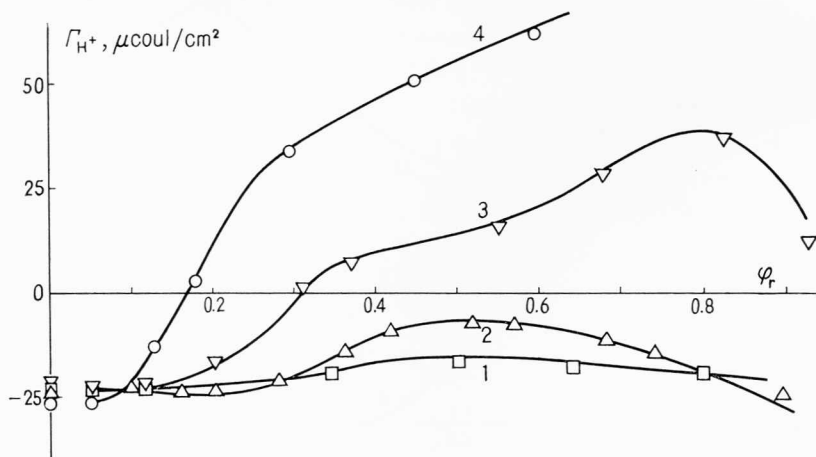


Fig. 2. Comparison of theoretically calculated (solid lines) and experimental (dots) dependences of Γ_{H^+} on φ_r on a Pt/Pt electrode in solutions: 1–0.01 N KOH, 2–0.01 N KOH + 1 N KCl, 3–0.01 N KOH + 1 N KBr, 4–0.01 N KOH + 1 N KI.

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TABLE 1.

Solution	$\varphi_{z.c.}$ V against (N. H. E.)		
	According to (1)	According to (2, 12)	Our measurements
1 N NaBr+ 5×10^{-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 CsCl+ 10^{-2} N CsOH	—	-0.55	—
1 N KI+ 10^{-2} N KOH	—	—	-0.52

*) This value was obtained in the presence of adsorbed hydrogen on the surface. According to^{2,12)} there is another pzc in the oxygen region at 0.3 V.

charge $\varphi_{z.c.}$ of platinum in alkaline solutions according to various authors.

Fig. 3 gives the anodic charging curves in investigated solutions and the curves of the dependence of the amount of hydrogen adsorbed on the electrode A_H on φ_r calculated by means of Eq. (3):

$$Q = \Gamma_{H^+} - A_H \quad (3)$$

The A_H , φ_r curve in 10^{-2} N KOH+1 N KI solution shows a vertical section corresponding to $A_H=0$. Thus the behavior of the Pt/Pt electrode in 10^{-2} N KOH+1 N KI solution is similar to that in 10^{-2} N HCl+1 N KCl solution.^{7,8)} There are no vertical sections on other curves, which is due to the overlapping of hydrogen and oxygen adsorption regions.

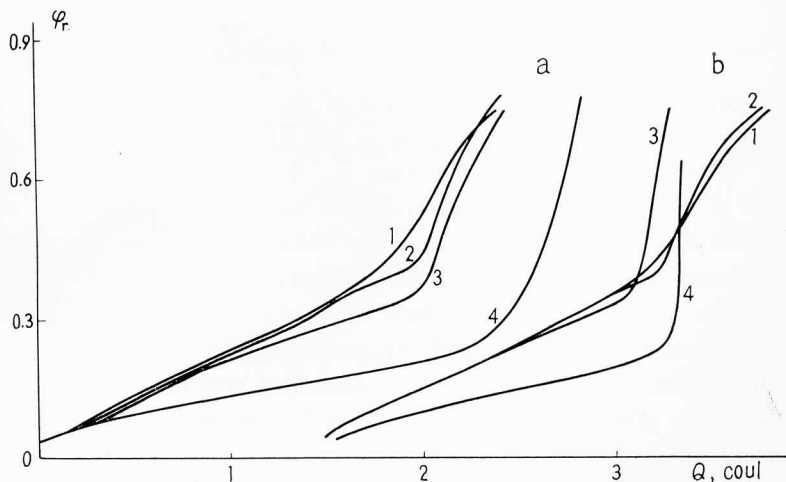


Fig. 3. Charging curves (a) and A_H , φ_r -curves (b) on a Pt/Pt electrode in solutions: 1-0.01 N KOH, 2-0.01 N KOH+1 N KCl, 3-0.01 N KOH+1 N KBr, 4-0.01 N KOH+1 N KI.

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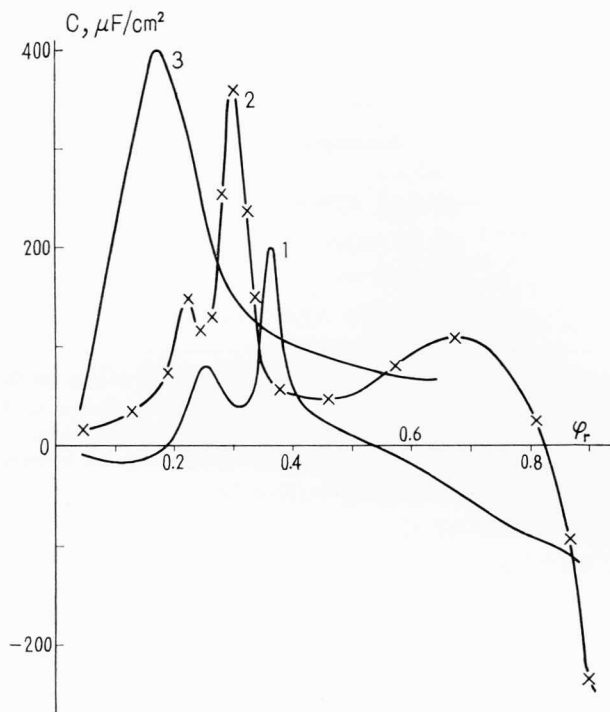


Fig. 4. Dependence of the equilibrium differential capacity of the double layer on φ_r on a Pt/Pt electrode in solutions: 1-0.01 N KOH+1N KCl, 2-0.01 N KOH+1 N KBr, 3-0.01 N KOH+1 N KI.

The curves of the equilibrium differential capacity¹¹⁾ $C = \left(\frac{\partial \varepsilon}{\partial \varphi_r} \right)_{\mu_{\text{OH}^-}, \mu_{\text{Cl}^-}}$ of the electric double layer obtained by means of Eq. (2) are given in Fig. 4. At the potentials of the double layer region in 1N KI + 10^{-2} N KOH solution the capacity is $\sim 70 \mu\text{F}/\text{cm}^2$. With decreasing φ_r , the C, φ_r -curve passes through a maximum at the potentials of the hydrogen region, this maximum being as high as $\sim 400 \mu\text{F}/\text{cm}^2$. Such high capacity values are due to the process of the displacement of anions by adsorbed hydrogen dipoles.^{11,13)}

The results in Fig. 2 permit to draw the conclusion about the applicability of the thermodynamic theory of the hydrogen electrode³⁾ to the Pt/Pt electrode in alkaline solutions. Earlier a similar conclusion was drawn in the case of measurements on platinum in acid solutions^{7,8,11)} as well as on rhodium,¹¹⁾ ruthenium and a platinum-ruthenium alloy.^{11,14)}

The value of Γ_{H^+} in alkaline solutions determined in the present paper as well as obtained by other methods in^{1,2,12)}, in the absence of specifically adsorbed anions depends but little on φ_r . This fact appears to be due to an

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accidental compensation of two effects: the adsorption of cations associated with H_{ads} ionization decreasing with increasing φ_r and the adsorption by hydrated surface oxide groups increasing within some range of φ_r .⁶⁾ This form of adsorption can be treated as an adsorption of ONa^- anions (or O_2Ba^{2-} anions in the case of doubly charged cations¹⁵⁾). Specifically adsorbed anions displace ONa^- anions from the surface, which results in a significant change of the shape of the Γ_{H^+} , φ_r -curve.

It follows from the comparison of $\varphi_{\text{z.c.}}$ in alkaline bromide given in Table 1 with $\varphi_{\text{z.c.}}$ in 10^{-2} N KBr + 1 N NaBr solution, found equal to -0.02 V in,¹⁾ that the p.z.c. of platinum shifts with changing solution pH in the presence of Br^- ions, this shift ranging according to various authors from 0.25 to 0.35 V. As was pointed out in the literature^{3,6)} the p.z.c. of metals adsorbing hydrogen and oxygen can shift with changing solution pH. Let us consider this problem in more detailed. From the Gibbs equation as applied to the hydrogen electrode in the presence of an excess of indifferent electrolyte^{3,7)}

$$d\sigma = \Gamma_{\text{H}} d\varphi_r - \Gamma_{\text{H}^+} d\mu_{\text{H}^+} \quad (4)$$

it follows that

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

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

or

$$\left(\frac{\partial \varphi_r}{\partial \mu_{\text{H}^+}} \right)_{\Gamma_{\text{H}^+}} = \left(\frac{\partial \Gamma_{\text{H}^+}}{\partial \Gamma_{\text{H}}} \right)_{\varphi_r} \quad (7)$$

In the above relations σ is the free surface energy per cm^2 , Γ_{H} —the Gibbs adsorption of hydrogen, μ_{H^+} —the chemical potential of H^+ ions. According to the model of the double layer structure on platinum given in Refs. 3) and 7) Eq. (7) expresses the shift of φ_r with pH at constant double layer charge. Taking into consideration Eq. (3), Eq. (7) can be written as:

$$\left(\frac{\partial \varphi_r}{\partial \mu_{\text{H}^+}} \right)_{\Gamma_{\text{H}^+}} = \frac{1}{\left(\frac{\partial A_{\text{H}}}{\partial \Gamma_{\text{H}^+}} \right)_{\varphi_r} - 1} = \frac{1}{\left(\frac{\partial A_{\text{H}}}{\partial \mu_{\text{H}^+}} \right)_{\varphi_r} : \left(\frac{\partial \Gamma_{\text{H}^+}}{\partial \mu_{\text{H}^+}} \right)_{\varphi_r} - 1} \quad (8)$$

or

$$\left(\frac{\partial \varphi_r}{\partial \mu_{\text{H}^+}} \right)_{\Gamma_{\text{H}^+}} = \left(\frac{\partial \varphi_r}{\partial \mu_{\text{H}^+}} \right)_{\Gamma_{\text{H}^+}} + 1 = \frac{\left(\frac{\partial A_{\text{H}}}{\partial \Gamma_{\text{H}^+}} \right)_{\varphi_r}}{\left(\frac{\partial A_{\text{H}}}{\partial \Gamma_{\text{H}^+}} \right)_{\varphi_r} - 1} \quad (8a)$$

where φ is the potential measured against N.H.E. The analysis of Eqs. (8) and (8 a) permits to estimate the possible values of $\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{r_{H^+}}$.

It follows from Eqs. (8) and (8 a) $\left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{r_{H^+}} = -1$ or $\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{r_{H^+}} = 0$, i.e. $\varphi_{z.c.}$ does not depend on pH, if $\left(\frac{\partial A_H}{\partial\mu_{H^+}}\right)_{\varphi_r} = 0$ and, in particular, at $A_H = 0$.

This conclusion is supported by measurements on metals not adsorbing hydrogen, e.g. on mercury.¹⁶⁾ Recently BALASHOVA *et al.*¹⁷⁾ using the radioactive tracers technique found $\varphi_{z.c.}$ of platinum to be independent of pH in $H_2SO_4 + Na_2SO_4$ solutions within pH range from 2 to 5. In the solutions investigated $\varphi_{z.c.}$ of platinum is located in that range of φ_r in which, as far as can be judged from the data in Ref. 3) the condition $\left(\frac{\partial A_H}{\partial\mu_{H^+}}\right)_{\varphi_r} = 0$ is approximately valid. This permits to explain the result obtained in Ref. 17).

BOCKRIS *et al.*¹⁸⁾ using the impedance method found the shift of $\varphi_{z.c.}$ of platinum in $HClO_4 + NaClO_4$ and $NaOH + NaClO_4$ solutions to correspond to the equation $\left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{\varphi=0} \approx 0$. However, the equality $\left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{r_{H^+}} = 0$ or $\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{r_{H^+}} = 1$ could be rigorously valid, as it follows from Eqs. (8) and (8 a), only in the case if Γ_{H^+} did not vary with A_H when μ_{H^+} changes and φ_r were constant, which is not the case in experiments. In fact, as it follows from the comparison of A_H , φ_r and Γ_{H^+} , φ_r -curves measured at different μ_{H^+} (in acid and alkaline solutions) generally speaking, the change of solution pH affects Γ_{H^+} more than A_H .

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