THE POTENTIAL OF CONSTANT CHARGE OF PLATINUM AND RHODIUM ELECTRODES AS A FUNCTION OF SOLUTION pH

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The dependence of the zero-charge potential, φ_{zc}, of a platinum electrode on solution pH was first established experimentally in [1] with measurements of adsorption curves in acidified and alkalized KBr solutions. It had been shown by Frumkin and Shlygin [2] that this dependence was caused by the dipole character of the bond of adsorbed hydrogen with the electrode surface. However, quantitative data on the effect of solution pH on the zero-charge potentials of metals that adsorb hydrogen and oxygen are few and contradictory, so that further studies are required for this problem.

Thus, Kheifets and Krasikov [3] conclude from the position of the differential-capacity minimum for the platinum electrode that φ_{zc} depends strongly on pH. Their conclusions were qualitatively confirmed by Gileadi, Argade, and Bockris [4] who with the same method found that in $HClO_4 + NaClO_4$ and $NaOH + NaClO_4$ solutions φ_{zc} shifts by 58 mV to the negative side when the pH is raised by 1. The results of this work and their analysis were criticized in [5, 6] on the basis of theoretical considerations. Subsequently Balashova and co-workers [7] did not observe pH dependence for φ_{zc} on a Pt/Pt electrode using radioactive tracers in $H_2SO_4 + Na_2SO_4$ solutions having pH between 2 and 5 and a total concentration between 10^{-2} and 10^{-3} N.

In the present work the effect of solution pH on potentials corresponding to constant double-layer charge was studied for platinum and rhodium in the following systems: the Pt/Pt electrode in solutions of $H_2SO_4 + Na_2SO_4$ (pH 1.60-3.74), HCl + 1 N KCl (pH 1.20-3.34), HBr + 1 N KBr (pH 1.15-3.15), and KOH + 1 N KBr (pH 10.3-12.3), and the rhodium-plated electrode in solutions of H_2SO_4 + 1 N Na_2SO_4 (pH 1.67-3.55). The methods of adsorption curves and of isoelectric potential shifts were used in the work. The measuring technique was described in [8]. In the same paper and in [9] the methods for electrode preparation and for the determination of their true surface areas were presented. The electrodes were chosen in such a way that independently of pH the maximum variation of hydrogen ion concentration did not exceed 20%. The accuracy of determination of hydrogen ion adsorption Γ_{H^+} was ± 1-2 $\mu C/cm^2$, the accuracy of determination of the potentials of zero charge was ±10 mV. The experiments were carried out at 20 ± 1°C, and φ_r denotes potentials referred to the reversible hydrogen electrode in the same solution.

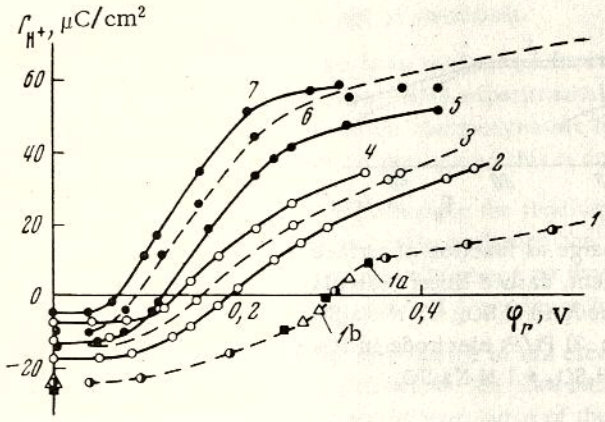

Fig. 1. Hydrogen ion adsorption as a function of potential for a Pt/Pt electrode in the solutions: KOH + 1 N KBr at pH 12 (1), 12.3 (1a), and 10.3 (1b); HCl + 1 N KCl at pH 3.24 (2), 2.0 (3), and 1.2 (4); HBr + 1 N KBr at pH 3.15 (5), 2.0 (6), and 1.15 (7). The dashed lines were calculated from the isoelectric potential shifts and the charging curves.

Figures 1 and 2 show the hydrogen ion adsorption Γ_{H^+} as a function of electrode potential for the systems studied. In every case the adsorption curve referring to a solution of intermediate pH was obtained by two methods: by direct adsorption measurements and by calculation from the charging curves and isoelectric potential shifts [8]. Curves 1 and 3 of Fig. 1 and curve 5 of Fig. 2 were taken from [6, 8-10]. For the solutions 0.01 N H_2SO_4 + 1 N Na_2SO_4 and 0.01 N HBr + 1 N KBr on the Pt/Pt electrode, comparison between calculation and experiment was first made in the present work. The concept that one can analyze the Pt surface as an equilibrium system proves again correct in these cases, as follows from the data obtained. However, in acidified bromide solution the agreement between calculated and

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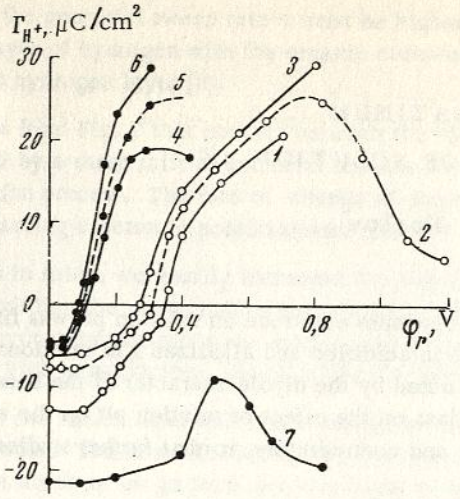

Fig. 2

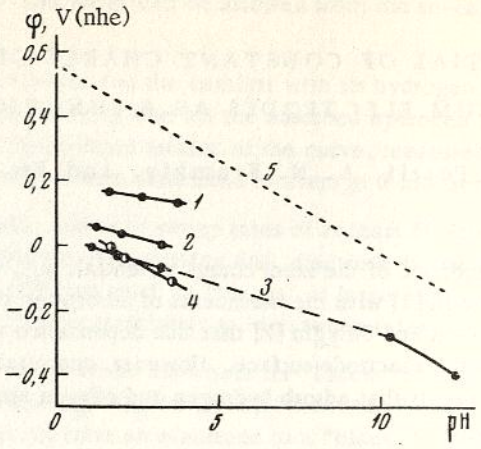

Fig. 3

Fig. 2. Hydrogen ion adsorption as a function of potential for a Pt/Pt electrode in the solutions: H_2SO_4 + 1 N Na_2SO_4 at pH 3.74 (1), 2.0 (2), and 1.6 (3); and NaOH + Na_2SO_4 at pH 12 (7); and for a rhodium electrode in the solutions: H_2SO_4 + Na_2SO_4 at pH 3.55 (4), 2.0 (5), and 1.67 (6). The dashed lines were calculated from the isoelectric potential shifts and the charging curves.

Fig. 3. Dependence of the points of zero charge on solution pH for a Pt/Pt electrode in H_2SO_4 + 1 N Na_2SO_4 (1), HCl + 1 N KCl (2), and HBr + 1 N KBr (3), and for rhodium in H_2SO_4 + 1 N Na_2SO_4 (4); 5) the dependence of pzc for platinum found in [4].

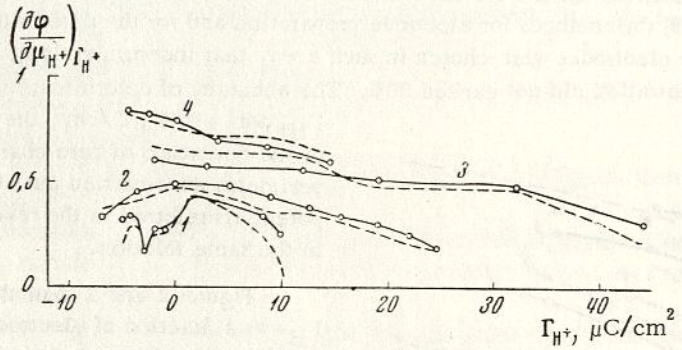

Fig. 4. The potential of constant charge as function of surface charge density (solid lines: experiment, dashed lines: calculation) for the systems: 1) Pt/Pt electrode in H_2SO_4 + 1 N Na_2SO_4; 2) Pt/Pt electrode in HCl + 1 N KCl; 3) Pt/Pt electrode in HBr + +1 N KBr; 4) rhodium electrode in H_2SO_4 + 1 N Na_2SO_4.

TABLE 1

Solution	$\varphi_{\Gamma_H = 0}$, in V(nhe)	φ_{zc}, in V(nhe)
1 *N* Na_2SO_4 + 0,01 *N* H_2SO_4	0,23	0,16
1 *N* Na_2SO_4 + 0,01 *N* NaOH	−0,25	—
1 *N* KCl + 0,01 *N* HCl	0,14	0,04
1 *N* KCl + 0,01 *N* KOH	−0,30	—
1 *N* KBr + 0,01 *N* HBr	0,06	−0,03
1 *N* KBr + 0,01 *N* KOH	−0,33	−0,39

experimental curves is limited to potentials φ_r not above ~0.35 V. At most anodic potentials some disagreement is observed. It seems that reversibility of the system is no longer a fully verified concept.

The results presented show that φ_{zc} for Pt and Rh when referred to a constant reference electrode shift to the negative side with increasing solution pH, with the magnitude of the shift depending on the nature of the electrode and the composition of the solution. Thus, for sulfate solutions on Pt the shift in φ_{zc} is about 18 mV per pH unit; for chloride solutions it is about 30 mV. The shift of φ_{zc} in acidified bromide solutions reaches ~35 mV and increases in alkaline solutions (Fig. 3). The largest shift in φ_{zc} with pH in acid solutions is observed on Rh. It is about 45 mV per pH unit.

Adsorption curves for the Pt/Pt electrode were also measured in H_2SO_4 + 0.1 N Na_2SO_4 solution. The same shift of φ_{zc} with pH was obtained as in solutions of H_2SO_4 + 1 N Na_2SO_4. We remark that the φ_{zc} shift with pH found for Pt in sulfate solutions is almost at the limit of accuracy of the technique used in [7].

The reliability achieved in determining the pH dependence of φ_{zc} in the present work can be checked in the the following way. As shown in [6], the shift of the potential of constant charge with solution pH can be expressed by Eq. (1):

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

where μ_{H^+} is the chemical potential of hydrogen ions, Γ_H is Gibbs surface excess of hydrogen. This equation can be rewritten in the following fashion:

$$\left(\frac{\partial \varphi}{\partial \mu_{H^+}}\right)_{\Gamma_{H^+}} = 1 + \left(\frac{\partial \Gamma_{H^+}}{\partial \mu_{H^+}}\right)_{\varphi_r} \Big/ \left[\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_Q \left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu_{H^+}}\right], \tag{2}$$

where φ is the potential measured with respect to a constant reference electrode, and $Q = -\Gamma_H$. The values of $(\partial\varphi/\partial\mu_{H^+})_{\Gamma_{H^+}}$ can be found directly from the experimental Γ_{H^+}-φ_r curves at different pH. They can, on the other hand, be calculated from Eq. (2) using the experimental Γ_{H^+} values at different pH and the results of independent measurements of isoelectric potential shifts and charging curves. The agreement between the experimental and calculated $(\partial\varphi/\partial\mu_{H^+})_{\Gamma_{H^+}}$ can serve as criterion for the correct experimental determination of the Γ_{H^+} values in solutions with different pH. It is important that one can in this way establish the correct mutual position of the adsorption curves over a wide range of potentials.

In Fig. 4 comparison has been made, as a function of surface charge density, between values of $(\partial\varphi/\partial\mu_{H^+})_{\Gamma_{H^+}}$ calculated from Eq. (2) and those found experimentally. The rather good coincidence of the curves indicates that the data obtained correspond to the thermodynamic relations. For the systems studied, $(\partial\varphi/\partial\mu_{H^+})_{\Gamma_{H^+}}$ goes to zero at large positive Γ_{H^+}, as seen in the figure; this is due to the approach toward the potential region of the double layer.

The large pH shift of φ_{zc} found for the rhodium electrode is in qualitative agreement with other experimental data. Thus, it was shown in [5] by analyzing the pH dependence of hydrogen adsorption that the contribution of the hydrogen atom to the potential difference on rhodium is considerably higher than on platinum. This may obviously be the cause for the greater pH dependence of φ_{zc} on rhodium.

Besides the potential of zero charge of the electric double layer, a potential corresponding to zero total surface charge, $\Gamma_H = 0$, can be defined for the platinum metals [8, 6]. This potential $\varphi_{\Gamma_H = 0}$ corresponds to the maximum of the equilibrium electrocapillary curve of the electrode [5]. The position of $\varphi_{\Gamma_H = 0}$ does not depend on models concerning the structure of the electrode-solution interface. Thus, $\varphi_{\Gamma_H = 0}$ is a more fundamental characteristic of an electrode that adsorbs hydrogen and oxygen than is φ_{zc}. A method for determining $\varphi_{\Gamma_H = 0}$ was given in [2]. In systems where the regions of hydrogen and oxygen adsorption overlap [10], $\varphi_{\Gamma_H = 0}$ can be obtained from experiments in which the test solution is replaced by a solution in which $\varphi_{\Gamma_H = 0}$ can be obtained from the intersection of the vertical straight line $A_H = 0$ (A_H being the quantity of adsorbed atomic hydrogen per cm^2 of the surface) with the charging curve. The value $\varphi_{\Gamma_H = 0}$ can also be determined in solutions such as Na_2SO_4 + NaOH where Γ_{H^+} does not go through zero at any φ_r and where, consequently, φ_{zc} lacks definition. Table 1 lists $\varphi_{\Gamma_H = 0}$ and φ_{zc} of the Pt/Pt electrode for a series of systems studied.

The values of φ_{zc} and $\varphi_{\Gamma_H = 0}$ depend, among others, on solution pH, and in solutions with weakly adsorbing anions, $\varphi_{\Gamma_H = 0}$ shifts more strongly with pH than φ_{zc}.

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