ADSORPTIVE PROPERTIES OF A PLATINUM ELECTRODE IN SOLUTIONS OF ACIDS WITHOUT THE ADDITION OF INDIFFERENT ELECTROLYTE

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The adsorptive properties of the Pt/Pt electrode in solutions of acids without additional indifferent electrolyte were first studied by Shlygin, Frumkin, and Medvedovskii [1] with the method of adsorption curves. Later [2, 3] some thermodynamic relations were examined which describe the behavior of a Pt electrode under the conditions considered here, and these relations were verified for the system: Pt/Pt electrode in 0.01 N HCl. The adsorption behavior of a Pt/Pt electrode in 0.01 N HBr and 0.01 N H_2SO_4 is investigated in the present work.

The expression for the total differential of the free surface energy, σ, for a hydrogen electrode in the solution of an acid H_nA is of the form ($\Gamma_{H_2O} = 0$):

$$d\sigma = -Q\,d\varphi_r - \Gamma_{H_nA}\,d\mu_{H_nA}, \tag{1}$$

where Q is the total surface charge [2, 3], Γ_{H_nA} and μ_{H_nA} are the surface excess and the chemical potential of the acid in electrical units, φ_r is the potential as referred to the reversible hydrogen electrode in the same solution. From (1) it follows that

$$(\partial Q/\partial\mu_{H_nA})_{\varphi_r} = (\partial\Gamma_{H_nA}/\partial\varphi_r)_{\mu_{H_nA}}, \tag{2}$$

$$(\partial\varphi_r/\partial\mu_{H_nA})_Q = -(\partial\Gamma_{H_nA}/\partial\varphi_r)_{\mu_{H_nA}}\ (\partial Q/\partial\varphi_r)_{\mu_{H_nA}}, \tag{3}$$

$$(\partial\varphi_r/\partial\mu_{H_nA})_{\Gamma_{H_nA}} = -(\partial\Gamma_{H_nA}/\partial\mu_{H_nA})_{\varphi_r}\ (\partial Q/\partial\mu_{H_nA})_{\varphi_r}, \tag{4}$$

$$(\partial\Gamma_{H_nA}/\partial\varphi_r)_Q = (\partial Q/\partial\mu_{H_nA})_{\Gamma_{H_nA}}. \tag{5}$$

For an acid HA, expression (3) can be written as

$$(\partial\varphi_r/\partial\mu^{\pm}_{HA})_Q = -2(\partial\Gamma_{HA}/\partial\varphi_r)_{\mu^{\pm}_{HA}}\ (\partial Q/\partial\varphi_r)_{\mu^{\pm}_{HA}}, \tag{6}$$

for an acid H_2A as

$$(\partial\varphi_r/\partial\mu^{\pm}_{H_2A})_Q = -3(\partial\Gamma_{H_2A}/\partial\varphi_r)_{\mu^{\pm}_{H_2A}}\ (\partial Q/\partial\varphi_r)_{\mu^{\pm}_{H_2A}}, \tag{7}$$

where $\mu^{\pm}_{HA}$ and $\mu^{\pm}_{H_2A}$ are the mean chemical potentials of the ions of the acid ($d\mu_{HA} = 2d\mu^{\pm}_{HA}$ and $d\mu_{H_2A} = 3d\mu^{\pm}_{H_2A}$) [3].

According to [3] one obtains the equations

$$(\partial\varphi/\partial\mu^{\pm}_{HA})_Q = 1 - 2(\partial\Gamma_{HA}/\partial\varphi)_{\mu^{\pm}_{HA}}\ (\partial Q/\partial\varphi)_{\mu^{\pm}_{HA}} \tag{8}$$

$$(\partial\varphi/\partial\mu^{\pm}_{H_2A})_Q = 1 - 3(\partial\Gamma_{H_2A}/\partial\varphi)_{\mu^{\pm}_{H_2A}}\ (\partial Q/\partial\varphi)_{\mu^{\pm}_{H_2A}}, \tag{9}$$

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from (6) and (7) when referring the electrode potential to a constant reference electrode, which is here designated by the symbol φ. Since $\Gamma_{HA} = \Gamma_{H^+} = \Gamma_{A^-}$ and $\Gamma_{H_2A} = \frac{1}{2}\Gamma_{H^+} = \frac{1}{2}\Gamma_{A^{2-}}$,* then

$$(\partial\varphi/\partial\mu^{\pm}_{HA})_Q = 1 - 2(\partial\Gamma_{H^+}/\partial\varphi)_{\mu^{\pm}_{HA}} \quad (\partial Q/\partial\varphi)_{\mu^{\pm}_{HA}}, \tag{10}$$

$$(\partial\varphi/\partial\mu^{\pm}_{H_2A})_Q = 1 - \frac{3}{2}(\partial\Gamma_{H^+}/\partial\varphi)_{\mu^{\pm}_{H_2A}} \quad (\partial Q/\partial\varphi)_{\mu^{\pm}_{H_2A}}. \tag{11}$$

Unlike the solutions containing excess inert electrolyte, which were predominantly studied previously [3], part of the H^+ ions in solutions of acid contribute to the formation of the ionic part of the double layer. Designating the surface excess of this part of the ions as $\Gamma^i_{H^+}$ we can write

$$\Gamma_{H^+} = \varepsilon + \Gamma^i_{H^+}, \tag{12}$$

where ε is the charge density on the metal side of the double layer. It follows from the theory of the electric double layer [4] that for a 1,1-valent electrolyte near the point of zero charge (pzc), $\Gamma_{C^+} = -\Gamma_{A^-} = -\frac{1}{2}\varepsilon$ in absence of specific adsorption, where Γ_{C^+} is the surface excess of the cation. Assuming that these conditions also prevail in our case we obtain $\Gamma_{H^+} = -\Gamma_{A^-} = -1/2\,\varepsilon$ and

$$(\partial\varepsilon/\partial\varphi_r)_{\mu^{\pm}_{HA}} = -(\partial\varphi_r/\partial\mu^{\pm}_{HA})_Q\,(\partial Q/\partial\varphi_r)_{\mu^{\pm}_{HA}}. \tag{13}$$

Thus, close to the pzc one can expect, in this approximation, that the pH variation of potential in pure acid is the same as that in the presence of an excess of neutral salt [3].

From Eqs. (8) and (9) one can derive a relation from which the Esin-Markov coefficient can be determined for platinum-group electrodes, Thus, substituting Q by $\varepsilon - A_H$ [2, 3] where A_H is the quantitity of atomic hydrogen adsorbed per cm^2 of surface in electrical units, and remembering that in pure acid

$$\varepsilon = \Gamma_{A^-} - \Gamma^i_{H^+}, \tag{14}$$

one can write

$$dQ = d\varepsilon - dA_H = d\Gamma_{A^-} - d\Gamma^i_{H^+} - dA_H, \tag{15}$$

$$\left(\frac{\partial\varphi}{\partial\mu^{\pm}_{HA}}\right)_Q = 1 + 2\left(\frac{\partial\Gamma_{A^-}}{\partial\varphi}\right)_{\mu^{\pm}_{HA}} \left[\frac{\partial(A_H - \Gamma_{A^-} + \Gamma^i_{H^+})}{\partial\varphi}\right]_{\mu^{\pm}_{HA}} = \left[\frac{\partial(A_H + \Gamma_{A^-} + \Gamma^i_{H^+})}{\partial(A_H - \Gamma_{A^-} + \Gamma^i_{H^+})}\right]_{\mu^{\pm}_{HA}} \tag{16}$$

At $A_H = 0$ the condition Q = const corresponds to ε = const, and Eq. (16) is transformed into

$$(\partial\varphi/\partial\mu^{\pm}_{HA})_\varepsilon = -(\partial\Gamma^i_{H^+}/\partial\varepsilon)_{\mu^{\pm}_{HA}} - (\partial\Gamma_{A^-}/\partial\varepsilon)_{\mu^{\pm}_{HA}}, \tag{17}$$

which coincides with the thermodynamic expression for the Esin-Markov effect that is known from the theory of electrocapillarity [4, 5]. However, in contrast to the case of mercury it is inapplicable at $\varepsilon = 0$ since the condition $A_H = 0$, as shown below, is realized on Pt only in HCl and HBr solutions over a limited range of positive φ_r.

Equations (8) and (9) were experimentally proven for 0.01 N HCl, HBr, and H_2SO_4 on a Pt/Pt electrode. Experimental details are described in [6]. Isoelectric potential shifts and adsorption curves in HBr solutions were measured on the same electrode, which had an apparent surface area of $s_{app} = 20$ cm^2 and a true area $s_{tr} = 2 - 1.5$ m^2. In HCl and H_2SO_4 solutions, charging curves and isoelectric shifts were measured on an electrode with $s_{app} = 20$ cm^2 and $s_{tr} = 1.5 - 2$ m^2, while Γ_{H^+} was determined with $s_{app} = 60$ cm^2 and $s_{tr} = 5 - 3$ m^2. The conditions of platinization and the roughness factor of large and small electrodes were approximately the same. The

*If Γ is expressed, not in electrical units but in moles, then $\Gamma_{H_2A} = \Gamma_{A^{2-}} = \frac{1}{2}\,\Gamma_{H^+}$.

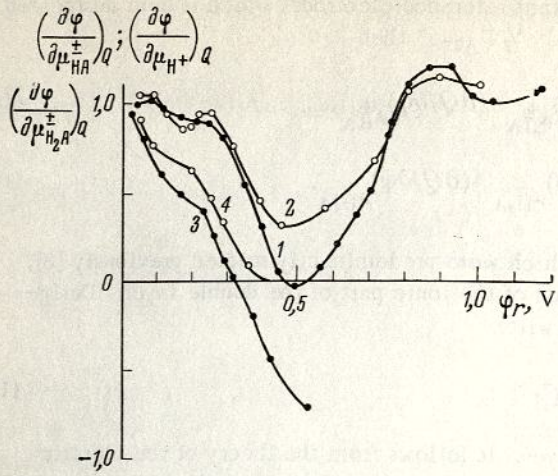

Fig. 1. Isoelectric potential shifts as functions of the potential of a Pt/Pt electrode in the solutions: 0.01 N H_2SO_4 (1); 0.01 N H_2SO_4 + 1 N Na_2SO_4 (2); 0.01 N HBR (3); and 0.01 N HBr + 1N KBr (4).

experiments were carried out at 20 ± 1°C. The time required for the potentials to stabilize during the measurements proves to be different for different acids and increases with the adsorbability of the acid's anion in the series H_2SO_4 < HCl < HBr. The isoelectric shifts were determined with both in going from 0.001 to 0.1 N solutions and in a narrower interval of pH change ($\Delta pH \simeq 1 - 1.3$), and concordant results were obtained.

Figures 1 and 2 compare $(\partial\varphi/\partial\mu^{\pm}_{HA})_Q$ and $(\partial\varphi/\partial\mu^{\pm}_{H_2A})_Q$ as functions of φ_r for the solutions of the acids with similar relations for acidified salt solutions already reported in the literature [6, 7]. At small φ_r the shifts are close to unity in all solutions, indicating that the derivative $\partial\Gamma_{H^+}/\partial\varphi_r$ is close to zero [3]. In a region of φ_r corresponding to small negative surface charges, i.e., near the pzc of platinum [3, 7], the potential variations in HCl and HBr solutions and in solutions with an excess of base electrolyte almost coincide, possibly because Eq. (13) is approximately satisfied. With increasing φ_r the derivatives diminish for all the solutions, though in different patterns. For acidified KCl and KBr solutions they become zero at $\varphi_r \gtrless 0.5$ and 0.4 V, respectively, since the equality $A_H = 0$ is fulfilled [2, 3]. In HCl and HBr solutions, $(\partial\varphi/\partial\mu^{\pm}_{HA})_Q$ goes through a minimum at these φ_r, reaching values close to −1 (the small deviation from −1 in HBr solutions is probably due to incomplete equilibration of the system at these φ_r). Thus, in the double-layer region the Pt/Pt electrode in solutions of acids practically behaves, under isoelectric conditions, as a reversible chloride or bromide electrode, i.e., its potential shifts by about 58 mV when the acid concentration is changed by one order of magnitude. This means that the Esin-Markov effect, which is due to the discrete structure of the double layer, is not observed on Pt when Cl^- and Br^- are adsorbed. According to [8], $(\partial\varphi/\partial\mu_{Br^-})_Q$ is close to −1 for φ_r values in the double-layer region, which also indicates absence of the Esin-Markov effect on Pt. In this respect the Pt electrode differs from the mercury electrode. The absence of an effect of discreteness can be explained by strong chemisorptive interaction between the adsorbed anions and the Pt surface, which leads to a merging of the anions' electron clouds and the metal's electron gas.* It must be noted that absence of the Esin-Markov effect also follows

*The Esin-Markov effect must vanish, according to the theory of the discrete double layer [10], when the distance between inner Helmholtz plane and the surface decreases.

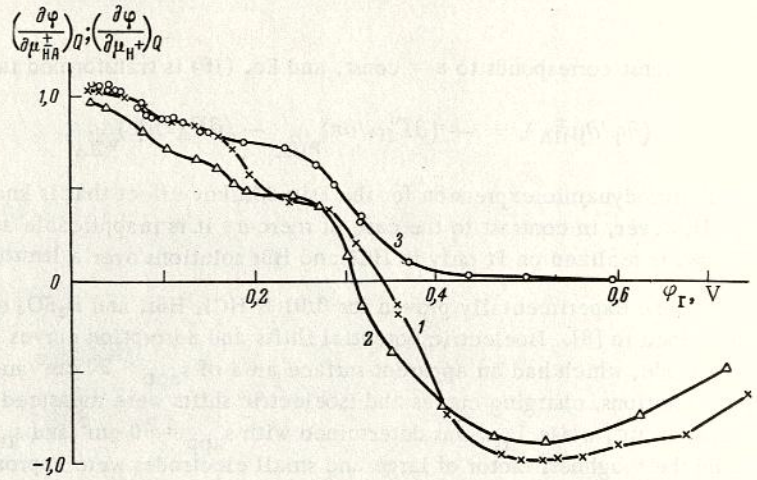

Fig. 2. Isoelectric potential shifts as functions of the potential of a Pt/Pt electrode in the solutions: 0.01 N HCl (1); 0.1 N HCl (2); and 0.01 N HCl + 1 N KCl (3).

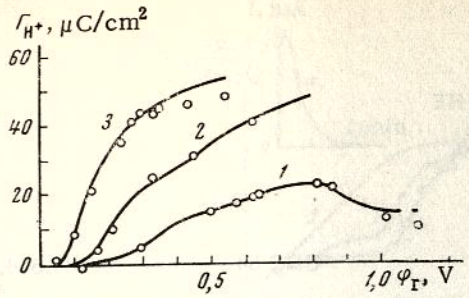

Fig. 3. Comparison of calculated (solid curves) and experimental (circles) adsorption curves for a Pt/Pt electrode in 0.01 N H_2SO_4 (1); 0.01 N HCl (2); and 0.01 N HBr (3).

from Balashova and Kazarinov's data [9], according to which cation adsorption in the double-layer region of potentials is practically independent of double-layer charge: $\partial\Gamma_{C^+}/\partial\varepsilon \sim 0$. It follows from Eq. (17) that the Esin-Markov effect then vanishes.

In H_2SO_4 solution, $(\partial\varphi/\partial\mu_{H_2A})_Q$ in the φ_r range considered is close to zero, while in acidified sulfate $(\partial\varphi/\partial\mu_{H^+})_Q > 0$, owing to the overlap of the hydrogen and oxygen adsorption regions. At more anodic φ_r the isoelectric shifts increases, owing to the adsorption of oxygen atoms. At sufficiently high φ_r, which can only be attained in H_2SO_4, $(\partial\varphi/\partial\mu^{\pm}_{H_2A})_Q$ becomes greater than unity, corresponding to a reduction in anion adsorption under the influence of oxygen adsorption. In fact, we obtain from Eqs. (8) and (9), taking into account Eq. (15):

$$(\partial\varphi/\partial\mu^{\pm}_{HA})_Q = 1 + 2\left[\left(\frac{\partial A_H}{\partial\Gamma_{A^-}}\right)_{\mu^{\pm}_{HA}} + \left(\frac{\partial\Gamma^i_{H^+}}{\partial\Gamma_{A^-}}\right)_{\mu^{\pm}_{HA}} - 1\right]^{-1}, \tag{18}$$

$$(\partial\varphi/\partial\mu^{\pm}_{H_2A})_Q = 1 + {}^3/_2\,[(\partial A_H/\partial\Gamma_{A^{2-}})_{\mu^{\pm}_{H_2A}} + (\partial\Gamma^i_{H^+}/\partial\Gamma_{A^{2-}})_{\mu^{\pm}_{H_2A}} - 1]^{-1}. \tag{19}$$

It can be seen from these relations that when $\partial\Gamma^i_{H^+}/\partial\Gamma_{A^-}$, $\partial\Gamma^{ij}_{H^+}/\partial\Gamma_{A^{2-}}$, $(\partial A_H/\partial\Gamma_{A^-})\mu^{\pm}_{HA}$, and $(\partial A_H/\partial\Gamma_{A^{2-}})\mu^{\pm}_{H_2A}$ equal zero, in particular when $A_H = 0$, then $(\partial\varphi/\partial\mu^{\pm}_{HA})_Q = -1$ and $(\partial\varphi/\partial\mu^{\pm}_{H_2A})_Q = -{}^1/_2$. When $A_H \neq 0$, i.e., when hydrogen or oxygen are present on the surface, then $1 > (\partial\varphi/\partial\mu^{\pm}_{HA})_Q > -1$ and $1 > (\partial\varphi/\partial\mu^{\pm}_{H_2A})_Q > -{}^1/_2$ so long as $(\partial A_H/\partial\Gamma_{A^-})\mu^{\pm}_{HA}$ or $(\partial A_H/\partial\Gamma_{A^{2-}})\mu^{\pm}_{H_2A}$ are less than zero. Since $(\partial A_H/\partial\Gamma_{An^-})\mu^{\pm}_{HnA} = (\partial A_H/\partial\varphi_r)\mu^{\pm}_{HnA}/(\partial\Gamma_{An^-}/\partial\varphi_r)\mu^{\pm}_{HnA}$ and since always $(\partial A_H/\partial\varphi_r)\mu^{\pm}_{HnA} < 0$, then the condition indicated is fulfilled when $\partial\Gamma_{A^-}/\partial\varphi_r$ and $\partial\Gamma_{A^{2-}}/\partial\varphi_r$ are larger than zero. In a certain potential region of oxygen adsorption, $\partial\Gamma_{A^-}/\partial\varphi_r$ and $\partial\Gamma_{A^{2-}}/\partial\varphi_r$ are less than zero and $(\partial A_H/\partial\Gamma_{A^{n-}})\mu^{\pm}_{HnA}$ consequently becomes a positive quantity. For $\partial A_H/\partial\Gamma_{A^-}$ and $\partial A_H/\partial\Gamma_{A^{2-}} > 1$, the isoelectric shifts must obviously exceed unity, as observed in sulfuric acid solutions.

Figure 3 compares experimental values of Γ_{H^+} with values calculated from Eqs. (8) and (9). The quantitative agreement between calculation and experiment confirms that it is correct to consider the platinum surface as an equilibrium system whose condition is determined by the independence variables μ_H and $\mu^{\pm}_{HA}$ or $\mu^{\pm}_{H_2A}$, and where for H_2SO_4 and HCl solutions this representation is true even for the initial part of oxygen adsorption. The divergence between calculation and experiment in HBr solutions at $\varphi_r > 350$ mV points to some irreversibility of Br^- adsorption, as observed in acidified KBr, too [7]. The adsorption curves obtained by us in solutions of acids agree with the data given in [1, 9].

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