ADSORPTION PROPERTIES OF RHODIUM AND PALLADIUM ELECTRODES IN ACID SOLUTIONS

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We have studied the adsorption behavior of a Rh electrode in 0.01 N HCl, HBr, and H_2SO_4 and of a Pd electrode in 0.01 N HCl, 0.01 N H_2SO_4, 0.01 N H_2SO_4 + 0.2 N Na_2SO_4, and 0.002 N H_2SO_4 + 0.1 N Na_2SO_4. The experiments were performed at 20 ± 1°C. The potentials φ_r refer to a reversible hydrogen electrode in the same solution, and the potentials φ to a constant comparison electrode.

According to thermodynamic theory, in acid solutions with no indifferent electrolyte [1],

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

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

where $\mu^{\pm}_{HA}$ and $\mu^{\pm}_{H_2A}$ are the mean chemical potentials of the acid ions, Q is the total surface charge [2, 3], and Γ_{H^+} is the hydrogen ion adsorption in the sense of Gibbs, which in these conditions can be equated to the adsorption of anions $\Gamma_A{}^{n-}$. The quantities Γ_{H^+} and μ are expressed in electrical units. The values of Γ_{H^+} for the rhodium electrode were calculated from the isoelectric potential shifts and charging curves by using (1) and (2), and were measured by a direct adsorption method. The experimental details are described in [4].

On Rh, measurements of the isoelectric potential shifts and Γ_{H^+} values were made on the same electrodes – in HCl and H_2SO_4 on an electrode with an apparent surface of 20 cm^2 and a true surface of 1-1.5 m^2, and in HBr on an electrode with an apparent surface of 40 cm^2 and a true surface of 2-2.5 m^2. The conditions of rhodium coating the electrodes were approximately identical. The true surfaces were determined as in [5]. The isoelectric shifts were measured for the transition from 0.005 N solutions to 0.02 N for HCl and H_2SO_4. For HBr, 0.0032 N solution was replaced by 0.032 N.

Figure 1 plots $(\partial\varphi/\partial\mu^{\pm}_{H_nA})_Q$ versus φ_r for a Rh electrode. For potentials in the hydrogen region, $(\partial\varphi/\partial\mu^{\pm}_{H_nA})_Q$ is nearly equal to unity, though less than for a Pt electrode [1]. This is evidently because anions are more strongly adsorbed on Rh than on Pt. When we go to the double-layer region, the values of $(\partial\varphi/\partial\mu^{\pm}_{HA})_Q$ for HCl and HBr decrease. For Rh in 0.01 N HCl + 1 N KCl, when $\varphi_r > 0.4$ V, there are no adsorbed hydrogen or oxygen atoms [6]. In 0.01 N HCl at 0.42-0.47 V, the value of $\partial\varphi/\partial\mu^{\pm}_{HA}$ is close to −1, which shows that the Esin-Markov effect is absent in this system [1]. The slight deviation from −1 can be attributed either to incomplete equilibrium of the system at these potentials, or to the fact that, at low concentrations, Cl^- anions do not completely displace adsorbed hydrogen and oxygen from the surface of the Rh electrode in the investigated range of φ_r.

In 0.01 N HBr the value of $\partial\varphi/\partial\mu^{\pm}_{HA}$ reaches a minimum at $\varphi_r \sim 0.43$ V, being only −0.4. Since it is unlikely that adsorbed gases are present on the Rh surface in the presence of Br^- ions, we must suppose that the system is already markedly irreversible at these potentials. This inference is supported by literature data [7].

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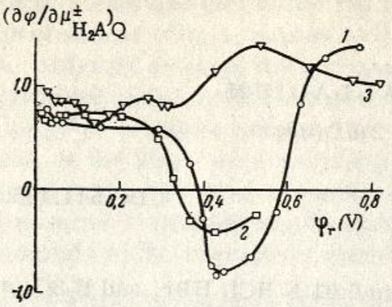

Fig. 1. Isoelectric potential shifts versus potential of Rh electrode in 0.01 N solutions: 1) HCl; 2) HBr; 3) H_2SO_4.

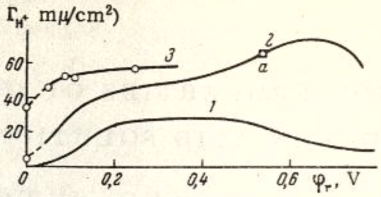

Fig. 2. Adsorption of hydrogen ions versus potential of Rh electrode in 0.01 N solutions of (1) HBr, (2) HCl, and (3) H_2SO_4. Solid curves: calculated; points: experimental values. a) Adsorption value used to determine constant of integration.

In 0.01 N H_2SO_4, even at $\varphi_r \sim 0.4$ V, $\partial\varphi/\partial\mu^{\pm}_{H_2A}$ becomes greater than 1; this corresponds to reduction in the adsorption of the anion under the influence of oxygen adsorption [1]. Thus on Rh in H_2SO_4 the regions of adsorption of hydrogen and oxygen overlap more markedly than on Pt; this has been previously observed for an acidulated solution of sodium sulfate [8].

Figure 2 plots the adsorption of anions on Rh versus potential, as calculated from (1) and (2), and also as found experimentally (points). From the curves it follows that for all the anions investigated, the adsorption at the φ_r of the hydrogen and double-layer regions is greater than for Pt; adsorption of Br^- and Cl^- is observed even at $\varphi_r = 0$. The explanation is that the zero-charge point of rhodium is more negative than that of platinum [8, 9]. Owing to the earlier adsorption of oxygen on rhodium, $\Gamma_{SO_4^{2-}}$ begins to decrease even at $\varphi_r \sim 0.4$ V. Decrease in Γ_{Cl^-}, due to oxygen adsorption, begins at $\varphi_r \sim 0.65$ V.

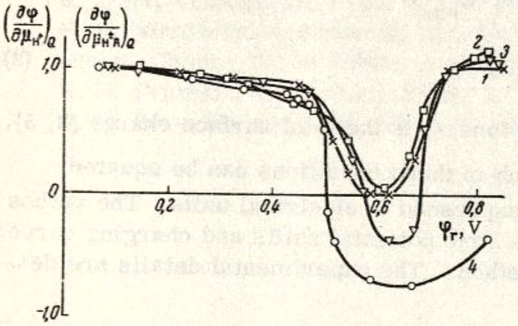

Fig. 3. Isoelectric potential shifts versus potential of Pd electrode in the following solutions: 0.01 N H_2SO_4 +0.2 N Na_2SO_4 (1); 0.002 N H_2SO_4 +0.1 N Na_2SO_4 (2); 0.01 N H_2SO_4 (3); and 0.01 N HCl (4).

The palladium-plated electrodes were prepared by precipitating Pd from 2% $PdCl_2$ solution, acidulated with HCl, on Pt foil or gauze. Deposition was carried out at a current density of 6 mA/cm² for about 30 min; after palladiumizing, the electrode was polarized cathodically, and before the experiments it was activated anodically and cathodically in 0.1 N H_2SO_4 at a current density of 5-10 mA/cm² for about 20 min. The isoelectric potential shifts and charging curves were measured on a palladium electrode with an apparent surface of 30 cm². Adsorption of H^+ was measured on an electrode with an apparent surface of 100 cm². The changes in the true electrode surface during the course of the work, together with the ratios between the surface areas of the various electrodes, were determined from the intercept of the charging curve from $\varphi_r = 80$ mV to $\varphi_r = 300$ mV according to [10].* During aging of the electrode we observed a decrease in the isoelectric shifts and also in the adsorption values, which decreased with time. We give results obtained from electrodes with stable surfaces.

Unlike other metals of the platinum group, Pd can dissolve appreciable amounts of hydrogen [11]. It has been shown [2] that, if we take account of the hydrogen dissolved in the bulk of the metal, for solutions with excess of indifferent electrolyte

$$(\partial\varphi/\partial\mu_{H^+})_{\Pi_H,\mu_{CA}} = 1 + (\partial\Gamma_{\mu^+}/\partial\varphi)_{\mu_{H^+},\mu_{CA}} : (\partial\Pi_H)\partial\varphi)_{\mu_{H^+},\mu_{CA}}, \tag{3}$$

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*Values of Γ_{H^+} for palladium are given in coulombs for the whole electrode. In recalculating these for unit true surface area, found by the method in [10], we found incomprehensibly low values of Γ_{H^+} and double-layer capacitances of one half to one third those on other platinum metals. Perhaps the method of determining the true surface area of Pd, described in [10], is not applicable to palladium-plated electrodes.

where $\Pi_H = v_S c_H - Q$ (v_S is the volume of the electrode per unit surface area and c_H is the volumetric concentration of hydrogen). Similarly (1) and (2) will take the form

$$(\partial\varphi/\partial\mu^{\pm}_{\mathrm{HA}})_{\Pi_H} = 1 + 2\,(\partial\Gamma_{H^+}/\partial\varphi)_{\mu^{\pm}_{\mathrm{HA}}} : (\partial\Pi_H/\partial\varphi)_{\mu^{\pm}_{\mathrm{HA}}}, \tag{4}$$

$$(\partial\varphi/\partial\mu^{\pm}_{\mathrm{H_2A}})_{\Pi_H} = 1 + \frac{3}{2}\,(\partial\Gamma_{H^+}/\partial\varphi)_{\mu^{\pm}_{\mathrm{H_2A}}} : (\partial\Pi_H/\partial\varphi)_{\mu^{\pm}_{\mathrm{H_2A}}}. \tag{5}$$

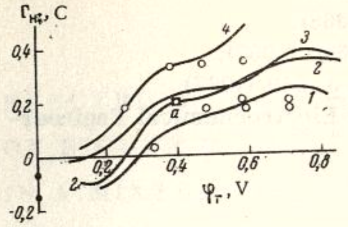

Fig. 4. Adsorption of hydrogen ions versus potential of Pd electrode in: 1) 0.002 N H_2SO_4 + 0.1 N Na_2SO_4; 2) 0.01 N H_2SO_4 + 0.2 N Na_2SO_4; 3) 0.01 N H_2SO_4; 4) 0.01 N HCl. Solid curves are theoretical; points are experimental values. a) Adsorption used in determining constant of integration.

Figure 3 plots $(\partial\varphi/\partial\mu_{H^+})_{\Pi_H, \mu_{CA}}$ versus φ_r- and $(\partial\varphi/\partial\mu^{\pm}_{H_nA})_{\Pi_H}$ versus φ_r for Pd. The isoelectric shifts were determined for acid concentration changes from 0.005 to 0.02 N. Curves 1 and 2 refer to solutions of H_2SO_4 in the presence of excess Na_2SO_4. In 0.01 N H_2SO_4 + 0.2 N Na_2SO_4 at $\varphi_r = 0.59$-0.63 V, $\partial\varphi/\partial\mu_{H^+} = 0$, which shows that adsorbed hydrogen and oxygen atoms are absent from the Pd surface at these potentials. Thus, in contrast to Pt, for Pd in sulfate solutions the regions of hydrogen and oxygen adsorption are not adjacent. Curve 2, which refers to 0.002 N H_2SO_4 + 0.1 N Na_2SO_4, passes somewhat higher than curve 1. Apparently the energy of the bonds linking hydrogen and oxygen atoms to the surface increases with the pH, leading to overlapping of their adsorption regions, although the quantities of adsorbed hydrogen and oxygen are small when $\varphi_r \sim 0.6$ V.

For 0.01 N H_2SO_4 at $\varphi_r \sim 0.65$ V, the derivative $\partial\varphi/\partial\mu^{\pm}_{H_2SO_4}$ reaches the value −0.4. According to thermodynamic theory, in the absence of the Esin-Markov effect, for H_2SO_4, on a surface free from adsorbed hydrogen and oxygen, we would expect the isoelectric shift to be equal to −0.5 [1]. From curve 4, referring to a Pd electrode in 0.01 N HCl, we see that for hydrochloric acid solutions $(\partial\varphi/\partial\mu^{\pm}_{HCl})_Q = 1$. This is due to solution of the Pd. The capacity of Pd to dissolve at anodic potentials in either hydrochloric or sulfuric acid is known from the literature [12, 13], and we confirmed it by analyzing the solution for Pd^{2+} ions with the aid of $SnCl_2$ [14].

Figure 4 plots Γ_{H^+} versus φ_r for the systems in question. The points indicate the experimental values of the adsorption. Adsorption values were calculated only for $\varphi_r > 100$-120 mV, because, owing to the increase in $\partial\Pi_H/\partial\varphi_r$, at lower φ_r values small errors in the isoelectric shift cause large errors in the calculated values of Γ_{H^+}.

From curve 2 it follows that the zero charge point of the double layer in 0.01 N H_2SO_4 + 0.2 N Na_2SO_4 on Pd lies at $\varphi_r \sim 0.25$ V, i.e., about 70 mV to the negative side of that for Pt in this solution; this agrees with the literature data [15, 16]. From curves 1 and 2 we see that as the pH increases, the zero-charge point, measured relative to a constant comparison electrode, shifts slightly towards negative potentials. It is difficult to draw quantitative conclusions on the shift of $\varphi_{z.c}$ with pH on the basis of the above data, owing to the narrow range of variation of the pH and the varying concentration of base electrolyte. The agreement between the calculated and experimental curves of Γ_{H^+} versus φ_r shows that (3), (4), and (5) apply to a palladium electrode. Discrepancies between theory and experiment occur at $\varphi_r > 0.6$ V for 0.002 N H_2SO_4 + 0.1 N Na_2SO_4, and even at $\varphi_r > 0.5$ V for 0.01 N HCl; they are probably due to solution of the Pd.

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