DEPENDENCE OF THE POTENTIAL OF CONSTANT DOUBLE-LAYER CHARGE ON SOLUTION pH FOR PLATINUM AND RHODIUM ELECTRODES IN THE OXYGEN ADSORPTION REGION

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The dependence of the potential of constant electric double-layer charge on solution pH was determined for platinum and rhodium in solutions of various composition in [4]. The measurements were made at the potentials of the hydrogen and the "double-layer" regions. In the present work similar measurements have been carried out at the potentials of oxygen adsorption at an electrode where the positive surface charge is reduced as the potential is shifted toward the positive side [2-4].

The experiments were made at 20 ±1°C on Pt/Pt and rhodium-plated electrodes in H_2SO_4 + 1 N Na_2SO_4 solutions at pH 1.60 to 3.74. The measuring technique, electrode preparation, and estimation of their true surface areas were the same as in [1]. The potentials φ_r refer to the reversible hydrogen electrode in the same solution, the potentials φ refer to the nhe.

The potential dependence of hydrogen ion adsorption, Γ_{H^+}, is shown in Figs. 1 and 2. According to [2, 4, 5] Γ_{H^+} equals the charge density on the metal side of the double layer. The shifts of the potential of constant double-layer charge during pH changes were obtained from the curves of Figs. 1 and 2. The systems studied are reversible in the initial section of oxygen adsorption [1, 6]; therefore, the quantities $(\partial\varphi/\partial\mu_{H^+})\Gamma_{H^+}$ can be calculated according to the thermodynamic relations of [1] utilizing the isoelectric potential shifts obtained in [1, 6]. The experimental and calculated values of $(\partial\varphi/\partial\mu_{H^+})\Gamma_{H^+}$ are given in Table 1 for various surface charge densities.

It is seen from the table that there is satisfactory agreement between calculation and experiment, indicating that the experimental data correspond to the thermodynamic relations. It follows from the results reported that the potentials of constant double-layer charge shift toward the negative side as the pH increases. The shift is about 150 mV for the rhodium electrode and about 80 mV for the platinum electrode per unit of pH change. Thus, the $(\partial\varphi/\partial\mu_{H^+})\Gamma_{H^+}$ in the oxygen adsorption region are considerably larger than those in the preceding portion of the $\Gamma_{H^+}-\varphi_r$ curve [1]. According to [7]

$$\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{\Gamma_{H^+}} = -\frac{X}{X+Y}\left[1+\left(\frac{\partial\mu_{H^+}}{\partial\varphi_r}\right)_Q\right], \quad (1)$$

where X is the atomic contribution, Y the ionic contribution to the potential drop, and Q the total surface charge; therefore, the increase in $(\partial\varphi/\partial\mu_{H^+})\Gamma_{H^+}$ at the potentials considered is obviously caused by the fact that in this case $(\partial\mu_{H^+}/\partial\varphi_r)_Q > 0$ and the ratio X/Y increases somewhat. This is confirmed by a calculation of the contributions of an oxygen atom, $X = (\partial\varphi/\partial A_0)\Gamma_{H^+}$, and a double layer ion, $Y = (\partial\varphi/\partial\Gamma_{H^+})A_0$, to the potential drop (A_0 is the amount of oxygen atoms per cm^2 of surface area in electrical units). The calculation was done in the same way as in [7]. The results of the calculation are given in Table 2.

At the potentials where Γ_{H^+} decreases with increasing φ_r, the contribution of an oxygen atom is about 4 to 5 times less than the contribution of a double-layer ion. However, owing to the difference in the maximum values of A_0 and Γ_{H^+} the total contribution of oxygen atoms is comparable in magnitude to the total

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TABLE 1. Values of $(\partial\varphi/\partial\mu_{H^+})\Gamma_{H^+}$

Electrolyte	Γ_{H^+}, $\mu C/cm^2$	$(\partial\varphi/\partial\mu_{H^+})\Gamma_{H^+}$ expt.	calc.	Electrolyte	Γ_{H^+}, $\mu C/cm^2$	$(\partial\varphi/\partial\mu_{H^+})\Gamma_{H^+}$ expt.	calc.
Rh	18	2,7	2,0	Pt/Pt	21	1,3	1,5
	16	2,7	2,1		20	1,3	1,4
	14	2,7	2,4		19	1,2	1,5
	13	2,6	2,6				

TABLE 2. The Calculated Values of X and Y

Electrolyte	Γ_{H^+}, $\mu C/cm^2$	φ_r, V	X, $cm^2/\mu F$	Y, $cm^2/\mu F$
Pt/Pt	20	0,92	0,0041	0,017
	19	0,94	0,0035	0,017
Rh	16	0,62	0,0031	0,012
	14	0,64	0,0025	0,011
	13	0,66	0,0023	0,011

TABLE 3. Values of the Potentials $\varphi_{Q=0}$ and φ_{zc}

Electrolyte	Solution	$\varphi_{Q=0}$, mV	φ_{zc}, mV
Rh	0.01*N* H_2SO_4 + 1*N* Na_2SO_4	50	—60
	0.01*N* NaOH + 1*N* Na_2SO_4	—400	—
	0.01*N* HCl + 1*N* KCl	0	—120

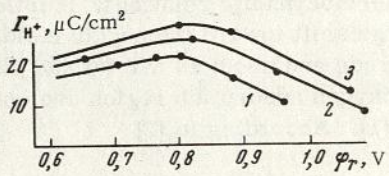

Fig. 1

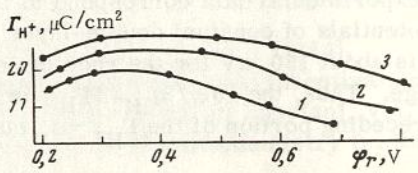

Fig. 2

Fig. 1. Potential dependence of hydrogen ion adsorption on a platinum electrode in H_2SO_4 + 1 N Na_2SO_4 at pH: 1) 3.74; 2) 2.6; 3) 1.60.

Fig. 2. Potential dependence of hydrogen ion adsorption on a rhodium electrode in H_2SO_4 + 1 N Na_2SO_4 at pH: 1) 3.74; 2) 2.60; 3) 1.67.

contribution of the ions, which causes a decrease in the adsorption of anions with increasing positive potentials. The positive value of $(\partial\varphi/\partial A_0)\Gamma_H$ means that the oxygen dipole is directed with the negative end toward the solution, as it is at less anodic potentials [7, 8].

In [1, 4, 5] the significance of the potential $\varphi_{Q=0}$ was discussed, which corresponds to zero total surface charge for platinum-group metals. Values of $\varphi_{Q=0}$ for the platinum electrode in solutions of different composition were given in [1]. In the present work we have obtained $\varphi_{Q=0}$ on the rhodium electrode in the solutions 0.01 N H_2SO_4 + 1 N Na_2SO_4 and 0.01 N NaOH + 1 N Na_2SO_4. To this end these solutions were replaced under isoelectric conditions by a 0.01 N HCl + 1 N KCl solution for which $\varphi_{Q=0}$ had been established previously [9]. The values $\varphi_{Q=0}$ and the potentials of zero charge φ_{zc} as referred to the nhe, are given in Table 3.

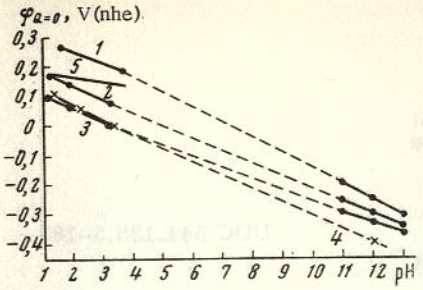

Fig. 3. The potential corresponding to zero total surface charge as a function of solution pH in sulfate (1), chloride (2), and bromide (3) solutions on platinum and in sulfate solutions on rhodium (4); 5) the pH dependence of the point of zero charge on platinum in sulfate solutions.

As on platinum, $\varphi_{Q=0}$ on rhodium is more positive than φ_{zc}. The values of $\varphi_{Q=0}$ on rhodium are more negative than those on the platinum electrode.

In [1] it has been shown that φ_{zc} and $\varphi_{Q=0}$ change differently with solution pH. The pH dependence of $\varphi_{Q=0}$ can be put together from the results of measuring isoelectric potential shift at changing pH and a starting potential of $\varphi_{Q=0}$. The relation thus obtained is shown in Fig. 3. In acid solutions the changes of $\varphi_{Q=0}$ with pH are larger than those of φ_{zc} [1]. For solutions of different composition, there are smaller differences in the changes of $\varphi_{Q=0}$ with pH for both platinum and rhodium than there are in the changes of φ_{zc}. In alkaline sulfate solutions on platinum the change of $\varphi_{Q=0}$ with pH increases and becomes approximately equal to that of the reversible hydrogen electrode potential. Using the relations given in [10] one can write

$$\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{Q=0} = \frac{1}{1-\left(\frac{\partial\Gamma_{H^+}}{\partial\varphi_r}\right)_{\mu_{H+}}\left(\frac{\partial\varphi_r}{\partial A_H}\right)_{\mu_{H+}}}, \qquad (2)$$

where A_H is the amount of atomic hydrogen adsorbed per cm^2 of surface area, in electrical units. Thus, the pH dependence of $\varphi_{Q=0}$ is determined by the relation between the derivatives $(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{H^+}}$ and $(\partial A_H/\partial\varphi_r)_{\mu_{H^+}}$ at this potential. The fact that $(\partial\varphi/\partial\mu_{H^+})_{Q=0} \simeq 1$ in alkaline solutions arises because in this case [1, 2] $(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{H^+}} \simeq 0$.*

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*It has been shown in [11] that the maximum adsorption of organic substances adsorbing reversibly on the platinum metals must to a first approximation occur close to $\varphi_{Q=0}$. In such a case the relation presented in Fig. 3 shows the variation in the potential of maximum adsorption with pH.