KINETIC BEHAVIOR OF ADSORBED HYDROGEN ON PLATINUM IN ALKALINE SOLUTIONS

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The published data about the kinetic behavior of adsorbed hydrogen on platinum in alkaline solutions in the region of anodic overpotentials are few and were obtained relatively recently [1-3]. On the basis of impedance measurements and measurements of the displacement of the cathodic charging curves with increase in the magnitude of the polarizing current it was concluded in these researches that the hydrogen reaction is less reversible in alkaline solutions than in the acidic solutions and that, with an excess of the indifferent electrolyte and with constant overpotential, its exchange current does not depend on the pH value. The last result has not been explained. Subsequently separate data were obtained on the kinetic behavior of adsorbed hydrogen in alkaline solutions [4, 5], but a systematic investigation was not undertaken. Recently Matsuda and Notoya [6] studied the cathodic evolution of hydrogen in alkaline solutions on vacuum-deposited films of platinum and proposed a mechanism involving the intermediate formation of atoms of alkali metal. In view of the possible transition of cations adsorbed on platinum metals to the adatom state [7, 8], a similar scheme cannot be rejected a priori for the region of anodic overpotentials.

In the present work the effect of pH and the composition of the solution on the behavior of adsorbed hydrogen on bright platinum in alkaline solutions was investigated by an impedance method. The measurements were made on a multifrequency vector polarograph, by means of which it was possible to record the components of the electrode admittance with linear variation of the electrode potential [9]. The potential variation rate amounted to 7 mV/sec. The experiments were carried out at 22 ± 2°C. The potentials referred to a reversible hydrogen electrode in the same solution are denoted by φ_r. The true surface area of the electrode was determined from the hydrogen section of the potentiodynamic curve in 1 N sulfuric acid on the calculation that the adsorption of hydrogen on 1 cm^2 amounts to 210 μC [10]. A preliminary report on the work was given in [11].

As shown by the experiments, reproducible values for the admittance components in alkaline solutions cannot be obtained if glass apparatus is used for the measurements and for preliminary purification and preparation of the solutions. The results depend to a large degree on the length of contact between the alkali and the glass and on the grade of glass. The reason is evidently dissolution of the glass and contamination of the solution of alkali with calcium cations. In fact, it was found that addition of calcium hydroxide to a solution of sodium hydroxide leads to a considerable change in the values of the capacitance (Fig. 1) and ohmic components of the admittance over the whole investigated range of potentials. Here the potentiodynamic curve for the platinum electrode only undergoes relatively small changes. Analogous results were obtained with additions of barium hydroxide. These data show that the exchange current of adsorbed hydrogen increases in the presence of alkaline-earth cations. In glass apparatus it was possible to obtain a series of C_s, φ_r curves intermediate between curves 1 and 2 in Fig. 1.

For this reason the following procedure was used for the measurements. The measurement part of the cell was made from quartz of optical purity. By special tests it was shown that the results are not affected by some dissolution of the quartz and entry of SiO_3^{2-} ions into the alkaline solution. Evidently, SiO_3^{2-} ions, like SO_4^{2-} and Cl^- ions [8, 12, 13], are not adsorbed on platinum in alkaline solution in the hydrogen region. The working electrode of platinum wire 50 μ thick was sealed into a glass capillary under vacuum. The solutions of the alkalis were prepared in the following way. The amalgam of the respective metal was

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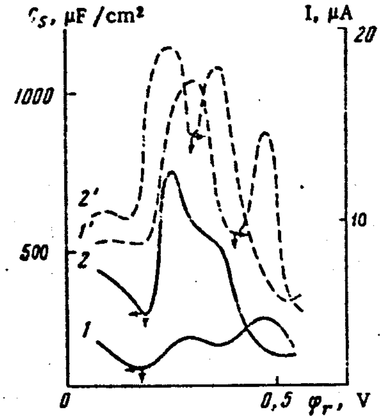

Fig. 1

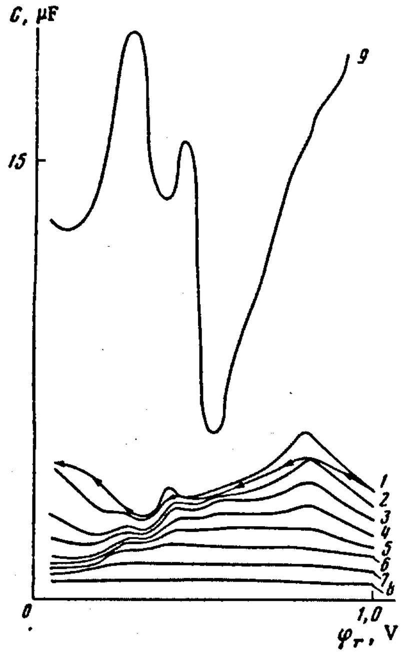

Fig. 2

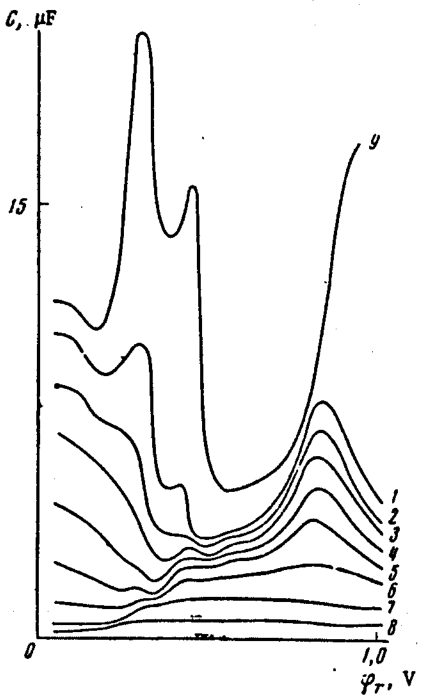

Fig. 3

Fig. 1. The dependence of C_s on potential in 0.01 N sodium hydroxide (1) and with addition of calcium hydroxide to a saturated solution (2) at frequency 40 Hz. The dashed lines represent the potentiodynamic curves in 0.01 N sodium hydroxide (1') and in the presence of calcium hydroxide (2') with a potential sweep rate of 0.5 V/sec.

Fig. 2. Dependence of C_p on potential in 1 N sodium sulfate solution (pH 11) at 40 (1), 80 (2), 160 (3), 320 (4), 600 (5), 1200 (6), 2400 (7), and 5000 (8) Hz. 9) Potentiodynamic curve in 1 N sodium sulfate solution with a potential sweep rate of 0.5 V/sec.

Fig. 3. Dependence of C_p on φ_r in 0.5 N cesium sulfate solution (pH 11) at 40 (1), 80 (2), 160 (3), 320 (4), 600 (5), 1200 (6), 2400 (7), and 5000 (8) Hz. 9) Potentiodynamic curve in 0.5 N cesium sulfate solution with potential sweep rate 0.5 V/sec.

prepared from mercury, which had been twice distilled under vacuum, and special-purity alkali. The amalgam was carefully washed and then partly decomposed in triply distilled water in quartz or Teflon cells. Subsequent purification of the alkali solution was realized by cathodic polarization for several days at a Pt/Pt gauze in a quartz cell. Alkaline solutions of the salts were obtained by electrolysis in a quartz cell with separated platinum cathode and anode. After twofold recrystallization the salts (lithium sulfate, sodium sulfate, potassium sulfate, cesium sulfate, sodium chloride, sodium bromide, and sodium iodide) were calcined immediately before the experiment (sodium iodide in an atmosphere of hydrogen). The calcium and barium hydroxides were purified by twofold recrystallization.

As an example, Figs. 2 and 3 show the experimental relations between the capacitance C_p and φ_r with various alternating current frequencies ν_i in 1 N sodium sulfate and 0.5 N cesium sulfate solutions which had been made alkaline to pH 11. The arrowed line shows the dependence on φ_r for the capacitance C_0 calculated from the almost-equilibrium potentiodynamic curve by means of the equation $C_0 = I/V$, where I is the current under potentiodynamic conditions and V is the potential sweep rate. The V values were selected in the range where the potentials of the maxima on the potentiodynamic curves do not depend on V ($V < 1$ V/sec according to [5]). The C_0 values can be regarded as the C_p values for $\omega \rightarrow 0$. Qualitative comparison of the C_p, φ_r relations shown in Figs. 2 and 3 indicates a considerable increase in the reversibility of the reaction involving deposition and removal of adsorbed hydrogen in the presence of Cs^+ ions compared with Na^+ ions. From these data it is also seen that hysteresis is observed between the curves measured with variation of the potential in the anodic and cathodic directions, and this is particularly significant in the oxygen region of φ_r. If the electrode reached φ_r values > 0.8 V during the anodic potential sweep, in the hydrogen region of φ_r the C_p and also the $1/R_p$ values were then higher than at electrodes which had previously been held at $\varphi_r = 40$ mV. Evidently, the small amounts of adsorbed hydrogen which did not succeed

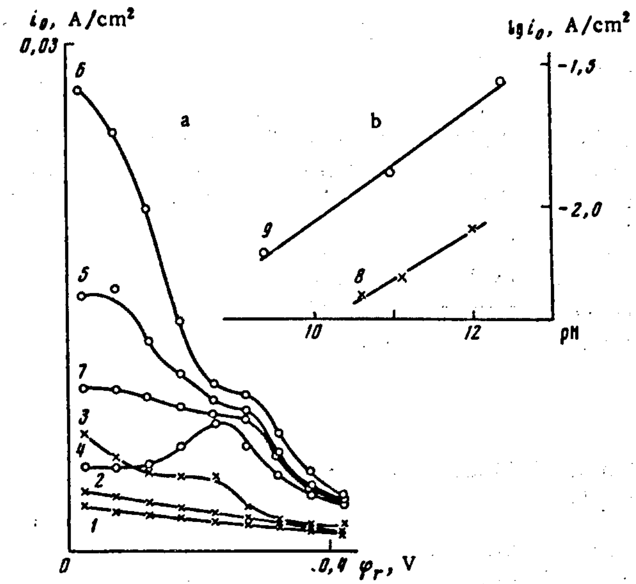

Fig. 4. a) Dependence of exchange current of adsorbed hydrogen on potential and pH of solution: in 1 N sodium sulfate (1-3, 8) with pH 10.6 (1), 11.1 (2), 12.0 (3); in 0.5 N cesium sulfate (4-6, 9) with pH 9.2 (4), 11.0 (5), 12.4 (6); in 0.02 N cesium sulfate with pH 11 (7). b) Dependence of logarithm of exchange current of hydrogen reaction at Pt electrode on pH in 1 N sodium sulfate (1) and 0.5 N cesium sulfate (2) for $\varphi_r = 40$ mV.

in being reduced during the cathodic potential sweep increase the exchange current of hydrogen at platinum in alkaline solutions. Steady C_p and $1/R_p$ values are established 1-2 min after return to $\varphi_r = 40$ mV. The C_p and $1/R_p$ values obtained during the anodic potential sweep after establishment of a steady state with $\varphi_r = 40$ mV were used for quantitative analysis. The C_p, φ_r, and $1/R_p$, φ_r curves obtained in lithium and potassium sulfate solutions are similar to those obtained in sodium sulfate solutions. Comparison of the C_p, φ_r, and $1/R_p$, φ_r curves obtained in alkaline solutions of lithium, sodium, potassium, and cesium sulfates and also in 0.1 N barium hydroxide solution shows that the reversibility of the hydrogen reaction increases in the order $Li^+ < Na^+ < K^+ < Cs^+ < Ba^{2+}$. The adsorbability of the inorganic cations on platinum in alkaline solutions, expressed in electrical units, increases in the same order [8, 12, 13]. In the case of acidic solutions increase in the specific adsorbability of the cations leads to decrease in the exchange current of the discharge of the ions and the ionization of the hydrogen atoms [14].

The effect of the nature of the supporting electrolyte anions on the exchange current in alkaline solutions was studied in alkaline solutions of 0.1 N sodium sulfate, sodium chloride, sodium bromide, and sodium iodide. The C_p, φ_r and $1/R_p$, φ_r curves obtained in the presence of sodium sulfate and sodium chloride almost coincided in the hydrogen region, since the SO_4^{2-} and Cl^- ions are not adsorbed on platinum in alkaline solutions in this region of φ_r [8, 12, 13]. In the presence of Br^- and particularly I^- the exchange current decreases, and with constant concentration of the salt the effect increases with decrease in the pH value.

The effect of the pH of the solution with a constant concentration of a salt having a surface-inactive anion is of particular interest. Measurements in 0.02 N and 1 N solutions of lithium, sodium, and potassium sulfate and also in 0.02 N and 0.5 N solutions of cesium sulfate at pH 9-12.5 show that with constant φ_r and a given frequency ν the C_p and $1/R_p$ values increase with increase in the pH value, i.e., the reversibility of the hydrogen reaction increases. From the measurements in solutions with identical pH values and different alkali-metal sulfate concentrations it is possible to conclude that the exchange current of adsorbed hydrogen increases with increase in the concentration of the indifferent electrolyte.

During quantitative analysis of the obtained data it was supposed that the behavior of the platinum electrode in alkaline solutions can be modelled to a first approximation by the Dolin–Érshler scheme [1]. The exchange currents were calculated by means of the equation

$$i_0 = \frac{RT}{F}\sqrt{\frac{C-C_1}{C_0-C}\cdot C_2^2\omega^2}, \qquad (1)$$

where C is the capacitance obtained in a parallel equivalent circuit with the given alternating-current frequency, C_1 is the double-layer capacitance, $C_2 = C_0 - C_1$, and $\omega = 2\pi\nu$. The capacitance at frequency 5 kHz was used for the double-layer capacitance. Equation (1) can be easily obtained from Eq. (8) in [1].

The exchange currents calculated by means of Eq. (1) for sodium sulfate and cesium sulfate solutions are given in Fig. 4. It is seen that the exchange current increases with increase in the pH of the solution and also with increase in the concentration of the salt at constant pH. The increase of the exchange current with increase in pH at $\varphi_r = 40$ mV corresponds to the equation

$$i_0 = K_1 c_{OH^-}^{0.30-0.33}, \qquad (2)$$

where c_{OH^-} is the concentration of OH^- ions and K_1 is a constant. In acidic solutions the exchange current decreases in proportion to $C_{OH^-}^{-0.5}$ [14].

The effect of the nature of the supporting electrolyte cations and anions and also the pH of the solution and the concentration of the indifferent electrolyte on the i_0 values can be explained if it is assumed that the formation and ionization of adsorbed hydrogen take place according to the equation $H_2O + \bar{e} \rightleftharpoons H_{ads} + OH^-$. The kinetic equation for this reaction can be represented in the following form [10, 14]:

$$i_0 = Kf(\theta)c_{OH^-}\exp\left\{\frac{(1-\alpha)F\varphi}{RT} + \frac{\alpha E\psi_1}{RT} - \frac{(1-\alpha)g_{ads}}{RT}\right\}, \qquad (3)$$

where $f(\theta)$ is some function of the degree of surface coverage with adsorbed hydrogen, g_{ads} is the free energy of adsorption of hydrogen, ψ_1 is the potential at the point where the center of the reacting particle is situated in the transition state, K and α are constants ($0 < \alpha < 1$), and φ is the potential referred to a constant reference electrode. According to the considerations in [10], in the region of average surface coverages with adsorbed hydrogen the dependence of i_0 on the composition of the solution is determined to a first approximation by the dependence of the ψ_1 potential on this parameter. Displacement of the ψ_1 potential towards the positive side during specific adsorption of cations or during increase in the concentration of a salt with a surface-inactive anion should lead to an increase in i_0, whereas a displacement of the ψ_1 potential to the negative side during specific adsorption of the anions should lead to a decrease in i_0. From Eq. (3) it also follows that $i_0 \sim K_1 c_{OH^-}^{\alpha}$ for constant φ_r, ψ_1, θ, and g_{ads} values. Comparison with the empirical equation (2) shows that at platinum in alkaline solutions $\alpha \approx 0.3$.

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