KINETICS OF THE EVOLUTION OF HYDROGEN ON SILVER FROM BUFFERED PHOSPHATE SOLUTIONS

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We had earlier studied the overvoltage of hydrogen on a silver cathode in sulfuric and hydrochloric and acidified solutions of the corresponding salts [1]. In this work, in order to expand the pH range, we investigated the question of the liberation of hydrogen from buffered solutions.

The preparation and procedure of the experiments was similar to those described in [1]. The measurements were performed at 25°C. Solutions of acid phosphates were used as the buffer system. The solutions were prepared from twice-recrystallized, calcined trisubstituted potassium phosphate (the selection of the salt and its preparation were recommended in the work of Bagotskii and Yablokova [2]), twice-redistilled sulfuric acid, and equilibrium tridistillate. Sulfuric acid was added in the amount required to create a solution with the necessary pH. The latter was determined with an accuracy within 0.05 with a tube pH meter with a glass electrode. A series of polarization curves in the pH range from 1.6 to 4.9 in solutions of 0.1 M $K_3PO_4 + H_2SO_4$ was obtained on the same electrode. The total concentration of univalent cations was 0.3 g-equiv /liter.

The results of the measurements are presented in Fig. 1. As can be seen from the figure, in solutions with a sufficiently high hydrogen ion concentration (curves 1 and 2), there is a distinct break on the polarization curve, separating the regions of normal and barrierless processes [1]. The dependence of the overvoltage for the lower and upper portions upon the hydrogen ion concentration is of a type corresponding to barrierless discharging, which turns into the usual form when the current density is increased. For higher pH values, sufficiently low current densities, necessary for the appearance of a transition from the usual discharging to the barrierless form, cannot be achieved. Curve 5 differs from the remaining curves in its kinetic characteristics. The curves taken at pH > 4.3 take approximately the same form as curve 5, but the overvoltage is smaller.

Figure 2 shows the dependence of the overvoltage on the pH of the solution at various current densities. As can be seen from the figure, the overvoltage increases as a linear function of the pH; however, the linearity is disrupted at pH > 3.3, which may be an indication of the change in the nature of the process. In a solution with pH < 3.3, the overvoltage, in general, obeys the function expressed by the equation:

$$\eta = a + \frac{1-\alpha}{\alpha}\psi_1 - \frac{1-\alpha}{\alpha}\frac{RT}{F}\ln[H_3O^+] + \frac{RT}{\alpha F}\ln i.$$

According to this equation, the overvoltage should change by approximately 59 mV when the pH changes by a unit with a constant total concentration of the solution. The quantity $(\partial\eta/\partial\,\mathrm{pH})_i$, found in this work, is 9-11 mV less than the theoretical. The following considerations can be brought in to explain this fact. At low pH values, the concentrations of the anions $H_2PO_4^-$ and SO_4^{-2} change greatly. Within the interval 1.6-2.2, this change is greater than within the interval 2.2-4.0. If we assume somewhat greater adsorbability of the $H_2PO_4^-$ anion in comparison with sulfate (this seems reasonable, since the solubility of silver phosphate is three orders of magnitude lower than that of the sulfate [3]), then at low pH, the value of the ψ_1-potential becomes less negative, which increases the overvoltage, and as a result, the slope of the curve in Fig. 2 is reduced (the increase in the overvoltage is especially appreciable for the lowest pH = 1.6). However, the deviations described are still small, and the dependence of the overvoltage on the pH is basically the same as in unbuffered solutions, close to the theoretical for the discharging of hydrogen ions.

In weakly acid and neutral buffer solutions, the kinetics of the process may be complicated by the fact that new proton donors appear, capable of participating in the discharging, such as, for example, nondissociated molecules of weak acids and anions of acid salts. In these solutions, in the region of potentials at which these measurements were performed, the surface carries a positive charge, as it follows from the literature data [4, 5]. It was

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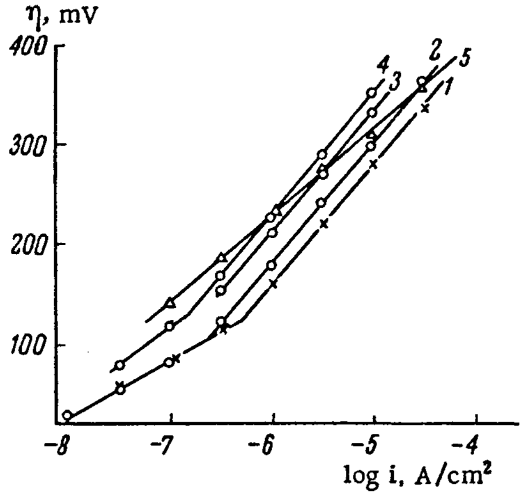

Fig. 1. Curves of overvoltage in solutions of 0.1 M K_3PO_4 + xMH_2SO_4; pH values of solutions: 1) 1.6; 2) 2.2; 3) 2.9; 4) 3.3; 5) 4.3.

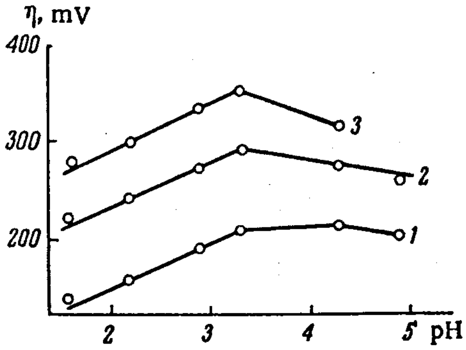

Fig. 2. Dependence of the overvoltage on the pH of the solution at current densities: 1) $10^{-6.2}$; 2) $10^{-5.5}$; 3) $10^{-5.0}$ A/cm².

noted earlier [1] that data on the overvoltage of hydrogen in sulfate and chloride solutions can be explained only considering the specific adsorption of anions on the positively charged surface. In this case, we should also assume specific adsorption of $H_2PO_4^-$ on the silver surface, which promotes discharging of the anion with a liberation of hydrogen. At a sufficiently low H^+ ion concentration, the rate of their discharging may be lower than the rate of discharging of $H_2PO_4^-$, since the latter is practically independent of the pH (the $H_2PO_4^-$ concentration depends very weakly upon the pH at pH around 4).

If we assume that the rate at pH ≥ 4 is determined by discharging of the anion of the acid salt, then the kinetic parameters should correspond to this process. The value of α found from the experiments for these curves is equal to 0.7.* This value may differ from the true value, because the apparent value of α depends greatly upon the structure of the electrical double layer, as is generally observed for the reduction of anions [6]. However, a quantitative consideration of this process is hindered, since it occurs against a background of other processes, in particular, at pH = 5, $HPO_4^{=}$ anions appear in appreciable amounts, which may influence the course of the electrode process.

Thus, in the region of pH < 3.5, there is chiefly a discharging of hydrogen ions, and $(\partial \eta / \partial \text{pH})_i$ in general corresponds to the theory of decelerated discharging. At higher pH, other proton donors take part in this process, which leads to a change in its kinetic characteristics.

At high current densities, when the potential approaches the point of zero charge, a sharp rise in the polarization curve is observed, analogous to that which Kolotyrkin observed for a number of other metals [7]. Calculations show that a violation of the Tafel dependence occurs as a result of a change in the kinetics of the electrode reaction, and not as a result of the ohmic potential drop in solution. For example, at $i = 10^{-0.3}$ A/cm², the ohmic potential drop under the conditions of our experiment cannot exceed 50 mV, while the deviation from the Tafel straight line at this current density comprises approximately 180 mV.

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* The shape of the polarization curve is influenced exclusively by the composition of the solution, since after curve 5, curves 3 and 1 were obtained on the same electrode.