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Abstract

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STUDY OF THE INFLUENCE OF THE STRUCTURE OF THE DOUBLE ELECTRIC LAYER ON THE REACTION OF ELECTROCHEMICAL DESORPTION

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The influence of the structure of the double electric layer on the hydrogen overvoltage on metals with a high overvoltage is one of the principal pieces of evidence for the irreversibility of the discharge reaction of the hydrogen ion or of the water molecule on the electrode surface, with subsequent formation of an adsorbed hydrogen atom. It seemed of interest to show experimentally the influence of the structure of the double electric layer on the reaction of electrochemical desorption,

$$H_{ads} + H^+ + e \rightarrow H_2 \quad \text{in an acidic medium,}$$

$$H_{ads} + H_2O + e \rightarrow H_2 + OH^- \quad \text{in an alkaline one.}$$

The present work is devoted to the investigation of this question. As was shown theoretically by A. N. Frumkin (^1), a measure of the rate of the electrochemical desorption reaction may be the magnitude of the decrease in the hydrogen overvoltage $\Delta\eta$ under the influence of atomic hydrogen diffusing to the electrode surface, at a given ratio of the flux of atomic hydrogen i', diffusing through a unit surface area of the electrode, to the current density of cathodic polarization of the electrode i_d. An increase in $\Delta\eta$ indicates an acceleration of the electrochemical desorption reaction; a decrease in $\Delta\eta$, its retardation.

In earlier works (^2) we showed that electrolytic atomic hydrogen, diffusing through an iron plate, lowers the hydrogen overvoltage in an alkaline solution on iron, on iron poisoned with lead and mercury, and on thin galvanic deposits of nickel, zinc, and tin applied to iron. The decrease in overvoltage at $i'/i_d = \text{const}$ increases with cathodic polarization of the electrode. In a sulfuric acid solution, an analogous action of diffusing atomic hydrogen on η was found only on iron poisoned with mercury or coated with a galvanic deposit of nickel; moreover, in the acid solution the effect of lowering the overvoltage on iron poisoned with

Figure 1

Figure 1: Figure 1

mercury was, in absolute magnitude, considerably smaller than in the alkaline solution (ˆ2). However, carrying out an investigation of the influence of the structure of the double electric layer on the electrochemical desorption reaction in an alkaline solution is difficult because of the difficulty of selecting substances capable of being adsorbed on the electrode from an alkaline solution at potentials corresponding to the hydrogen overvoltage. Therefore we attempted to detect the influence of the structure of the double electric layer on the electrochemical desorption reaction in acidic solutions. Measurements were carried out in $1N$ H_2SO_4 on iron, on whose surface J^- had been chemisorbed from the solution, and on iron poisoned with mercury. It is known that adsorption of halide anions on iron leads to an increase in the hydrogen overvoltage. This effect, by analogy with Pt and Pd (ˆ3), is explained by a decrease in the bond energy W of Me—H_{ads} upon adsorption of J^- on active sites of the electrode surface. The decrease in W, in turn, should facilitate the transition from the catalytic mechanism of removal $2H_{ads} \rightarrow H_2$ to the elec-

trochemical

$$H_{ads} + H^+ + e \rightarrow H_2.$$

Such a representation, as will be seen below, is confirmed experimentally. As surface-active cations that shift the ψ'-potential in the positive direction and thereby decrease the concentration of hydrogen ions in the electrical double layer, we chose tetrabutylammonium cations $(C_4H_9)_4N^+$ and La^{3+}. The apparatus, measurement procedure, and preliminary preparation of the electrodes remained the same (2). Measurements were carried out under cathodic polarization of the diffusion side of the electrode by a current $i_d = 5 \cdot 10^{-3}$ A/cm^2.

Figure 1 gives data on the influence of diffusing atomic hydrogen on η on iron in solutions of $1N$ H_2SO_4, $1N$ $H_2SO_4 + 1N$ KJ, and $1N$

Fig. 1. Influence of diffusing hydrogen on η on iron in solutions: I $-1N$ H_2SO_4, $i'/i_d \sim 0.8$; II $-1N$ $H_2SO_4 + 1N$ KJ, $i'/i_d \sim 0.8$; III $-1N$ $H_2SO_4 + 1N$ KJ+ sat. $(C_4H_9)_4$NJ, $i'/i_d \sim 0.8$.

$H_2SO_4 + 1N$ KJ+ sat. $(C_4H_9)_4$NJ. Along the abscissa axis, as also in the following figures, time in hours is plotted; along the ordinate axis–the hydrogen overvoltage. The points denote the values of η in the absence of diffusing hydrogen; the circles, in its presence. From Fig. 1 it is seen that, upon addition of KJ to a $1N$ H_2SO_4 solution, η increases by $\sim$ 160-180 mV, and that in such a solution diffusing hydrogen lowers η. Subsequent addition of $(C_4H_9)_4$NJ to $1N$ $H_2SO_4 + 1N$ KJ leads to an additional increase of η by

$\sim$ 80 mV; however, the decrease of the overvoltage under the influence of diffusing hydrogen at $i'/i_d \sim$ const proves to be smaller than the value observed in the $1N$ $H_2SO_4 + 1N$ KJ solution at lower values of η. Since $\Delta\eta$ at $i'/i_d =$ const is a measure of the rate of the electrochemical desorption reaction, it follows that adsorption of the $(C_4H_9)_4N^+$ cation slowed this reaction, as was to be expected, taking into account the decrease in the concentration of hydrogen ions in the double layer in the presence of $(C_4H_9)_4N^+$.

The influence of the $(C_4H_9)_4N^+$ cation on the rate of the electrochemical desorption reaction on iron poisoned with mercury in a $1N$ H_2SO_4 solution is shown in Fig. 2. The electrode under study was strongly poisoned with mercury, and η on it at $i_d = 5 \cdot 10^{-3}$ A/cm^2 was $\sim$ 700 mV higher than on pure iron. Diffusing atomic hydrogen lowered η on such an electrode by 45-50 mV. Upon addition to the $1N$ H_2SO_4 solution of $10^{-2}M$ $(C_4H_9)_4NBr$*, η on the electrode increased additionally by 100-110 mV, while the decrease of η under the influence of diffusing hydrogen fell to 15-20 mV. Thus, on iron poisoned with mercury as well, the $(C_4H_9)_4N^+$ cation raises η and lowers the rate of the electrochemical desorption reaction.

The La^{3+} cation has the same effect on the value of $\Delta\eta$ as the $(C_4H_9)_4N^+$ cation. On iron poisoned with Hg, in the presence of La^{3+} the value of $\Delta\eta$ substantially smaller than that observed in a solution of $1N$ H_2SO_4 not containing La^{3+} (Fig. 3).

We made an attempt to investigate the effect on $\Delta\eta$ of the simultaneous poisoning of iron by the ion J^- and by mercury; however, we did not detect any influence of J^- on the magnitude of the decrease in overvoltage during diffusion to the surface of atomic hydrogen on iron, both strongly and weakly poisoned with Hg. In the case of strong poisoning of the iron with Hg, the absence of such an effect could be explained by the high cathodic potential of the electrode, at which J^- is no longer adsorbed. This explanation agrees with the fact that J^- also has no effect on the value of η on iron strongly poisoned with Hg. However, on iron weakly poisoned with mercury, J^- increases η, which indicates its adsorption, but this does not affect the value of $\Delta\eta$. The reason for such behavior of J^- in this case remained unclear.

Fig. 2. Influence of diffusing hydrogen on η on iron strongly poisoned with mercury, in solutions:
I $-1N$ H_2SO_4, $i'/i_d \sim 0.4$;
II $-1N$ $H_2SO_4 + 0.01\,M$ $(C_4H_9)_4NBr$, $i'/i_d \sim 0.4$.

Fig. 3. Influence of diffusing hydrogen on η on iron strongly poisoned with mercury, in solutions:

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* The use of the bromide salt of tetrabutylammonium made it possible to have a higher concentration of the $(C_4H_9)_4N^+$ cation in solution (tetrabutylammonium iodide salts are very poorly soluble). From what follows it will be clear that introduction of Br^- into the solution could affect neither η nor $\Delta\eta$.

I $-1N$ H_2SO_4, section A $-i'/i_d \sim 0.4$, section B $-i'/i_d \sim 0.2$;
II $-1N$ H_2SO_4+ saturated $La_2(SO_4)_3$, section C $-i'/i_d \sim 0.1$, section B $-i'/i_d \sim 0.2$.

From the work carried out it follows that, on an iron electrode in a sulfuric acid solution in the presence of the ion J^- and upon poisoning of the electrode with Hg, the relative weight of the electrochemical mechanism of removal of H_{ads} increases in comparison with the catalytic one. Direct experiments have shown that, in accordance with the concept of the influence of the structure of the electrical double layer on the reaction of discharge of the hydrogen ion, the cations $(C_4H_9)_4N^+$ and La^{3+}, shifting the ψ'-potential in the positive direction, inhibit the reaction of electrochemical desorption. The influence of the structure of the electrical double layer on $\Delta\eta$, the magnitude of the decrease in η under the action of diffusing hydrogen, may be regarded as additional evidence that the observed decrease in overvoltage is associated with the occurrence, on the electrode surface, of the reaction of electrochemical desorption.

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Note: Figure translations are in progress. See original paper for figures.