AN INVESTIGATION OF ELECTROCHEMICAL DESORPTION AS AFFECTED BY THE STRUCTURE OF THE ELETRIC DOUBLE LAYER

N. A. Bagotskaya

Institute of Electrochemistry, Academy of Sciences USSR
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The effect which the structure of the electric double layer has on the hydrogen overvoltage on metals characterized by high overvoltages is one of the main proofs that the discharge of a hydrogen ion or water molecule on the electrode surface with the ensuing formation of adsorbed hydrogen is an irreversible reaction. It was of interest to demonstrate experimentally the effect of the structure of the electric double layer on the 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 paper is devoted to a study of this problem. As a measure of the rate at which the electrochemical desorption proceeds one may use, as has been shown theoretically by A. N. Frumkin [1], the drop, $\Delta\eta$, of the hydrogen overvoltage under the influence of atomic hydrogen diffusing to the electrode surface at a given ratio between the current i' of atomic hydrogen diffusing through unit electrode surface area and the current density i_d of cathodic electrode polarization. Increased $\Delta\eta$ points to acceleration of the electrochemical desorption; decreased $\Delta\eta$ to retardation of this reaction.

It was shown previously [2] that electrolytically produced atomic hydrogen, when diffusing through an iron slab, lowers the hydrogen overvoltage in an alkaline solution on iron, iron poisoned by lead or mercury and on thin galvanic films of nickel, zinc and tin deposited on iron. The lowering of the overvoltage at i'/i_d = const rises at increasing cathodic polarization of the electrode. In sulfuric acid solution the analogous effect of diffusing atomic hydrogen η was detected only on iron poisoned by mercury or covered by a galvanic nickel deposit and in an acid solution the lowering of the overvoltage on iron poisoned by mercury was of much smaller absolute magnitude than in an alkaline solution [2]. But the carrying out of investigations into the effect which the structure of the electric double layer has on electrochemical desorption in an alkaline solution is hampered by the difficulty of selecting substances which are able to be adsorbed from an alkaline solution at potentials corresponding to hydrogen overvoltage. Therefore, we attempted to reveal the effect which the structure of the electric double layer has on electrochemical desorption in acidic solutions. The measurements were carried out in 1 N H_2SO_4 on iron on the surface of which I^- had been chemisorbed from a solution and on iron poisoned by mercury. It is known that adsorption of halide ions on iron leads to a raised hydrogen overvoltage. This effect, in analogy to that on Pt and Pd [3], is explained by the decreased energy W of the Me-H_{ads} bond resulting from I^- adsorption on the active regions of the electrode surface. A decreased W, in its turn, should favor the transition from the catalytic mechanism of the hydrogen liberation $2H_{ads} \rightarrow H_2$ to the electrochemical mechanism $H_{ads} + H^+ + e \rightarrow H_2$. As will be seen below, this supposition is confirmed by the experiment. As surface-active substances shifting the ψ_1-potential into the positive direction and just thereby lowering the concentration of hydrogen ions in the electric double layer we have chosen the tetrabutylammonium $(C_4H_9)_4N^+$ and La^{3+} cations. The equipment, the procedure of the measurements and the pretreatment of the electrodes were kept the same as previously [2]. The measurements were done at cathodic polarization of the diffusional side of the electrode by a current density $i_d = 5 \cdot 10^{-3}$ amp/cm^2.

In Fig. 1 we give data on the effect which diffusing atomic hydrogen has on η on iron in the solutions 1 N H_2SO_4, 1 N H_2SO_4 + 1 N KI and 1 N H_2SO_4 + 1 N KI + sat. $(C_4H_9)_4NI$. Along the axis of abscissas, just as is done in the subsequent figures, time expressed in hours is plotted versus the hydrogen voltage as ordinates. By filled points

we designate the η values in the absence of diffusing hydrogen, by circles those found when diffusing hydrogen is present. From Fig. 1 it is evident that the addition of KI to a 1 N solution of H_2SO_4 raises η by about 160-180 mv and diffusing hydrogen in such a solution lowers η. Admixture of $(C_4H_9)_4NI$ to 1 N H_2SO_4 + 1 N KI gives an additional increase of η by about 80 mv, but the lowering of the overvoltage under the influence of diffusing hydrogen

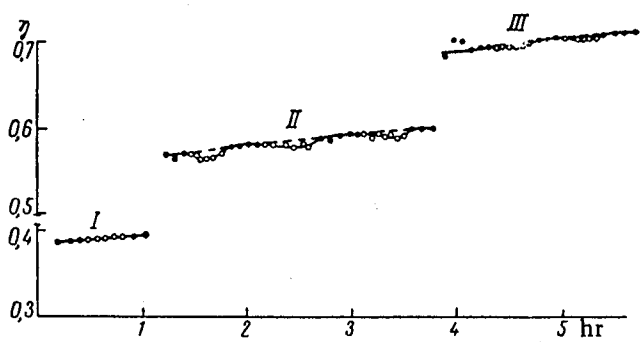

Fig. 1. The effect of diffusing hydrogen on η on iron in the solutions: I) 1 N H_2SO_4, $i'/i_d \sim 0.8$; II) 1 N H_2SO_4 + 1 N KI, $i'/i_d \sim 0.8$; III) 1 N H_2SO_4 + 1 N KI + sat. $(C_4H_9)_4NI$, $i'/i_d \sim 0.8$.

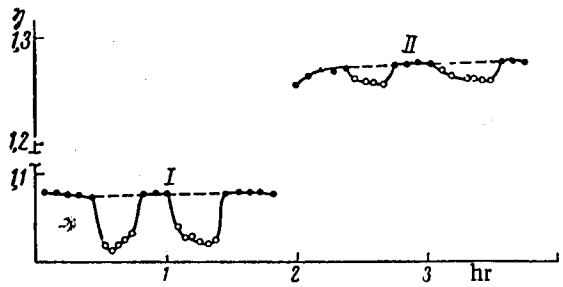

Fig. 2. The effect of diffusing hydrogen on η on iron strongly poisoned by mercury in the solutions: I) 1 N H_2SO_4, $i'/i_d \sim 0.4$; II) 1 N H_2SO_4 + 0.01 M $(C_4H_9)_4NBr$, $i'/i_d \sim 0.4$.

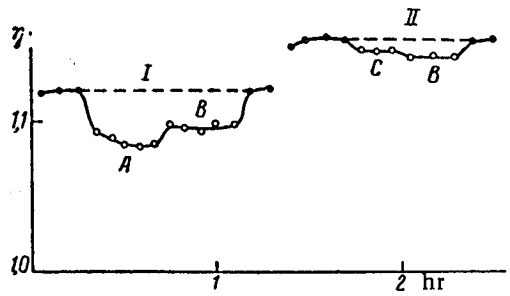

Fig. 3. The effect of diffusing hydrogen on η on iron strongly poisoned by mercury in the solutions: I) 1 N H_2SO_4, region A) $i'/i_d \sim 0.4$, region B) $i'/i_d \sim 0.2$; II) 1 N H_2SO_4 + sat. $La_2(SO_4)_3$, region C) $i'/i_d \sim 0.1$, region B) $i'/i_d \sim 0.2$.

at i'/i_d = const is found to be smaller than that observed in the 1 N H_2SO_4 + 1 N KI solution at lower values of η. Since $\Delta\eta$ at i'/i_d = const is a measure of the rate at which electrochemical desorption takes place, it follows from these data that adsorption of the cation $(C_4H_9)_4N^+$ retarded the said reaction, as should be expected, when one keeps in mind that in the presence of $(C_4H_9)_4N^+$ the concentration of hydrogen ions in the double layer is lowered.

In Fig. 2 we show the effect which in a 1 N H_2SO_4 solution the $(C_4H_9)_4N^+$ cation has on the electrochemical desorption on iron poisoned by mercury. The electrode examined had been strongly poisoned by mercury and at $i_d = 5 \cdot 10^{-3}$ amp/cm^2 its value of η was by about 700 mv higher than that on pure iron. Diffusing atomic hydrogen lowered η on this electrode by 45-50 mv. Upon adding 10^{-2} M $(C_4H_9)_4NBr$ to the 1 N H_2SO_4 solution the value of η on the electrode rose further by 100-110 mv and the lowering of η under the influence of diffusing hydrogen dropped to 15-20 mv. So, also on iron poisoned by mercury the $(C_4H_9)_4N^+$ cation raises η and lowers the electrochemical desorption rate.

* By using the bromide salt of tetrabutylammonium we were able to attain in the solution a higher concentration of $(C_4H_9)_4N^+$ cations (flakes of tetrabutylammonium iodide are difficulty soluble). From the rest of the paper it will be clear that introduction of Br^- to the solution cannot have an effect neither on η nor on $\Delta\eta$.

The La^{3+} cation has just the same effect on the magnitude of $\Delta\eta$ as does the $(C_4H_9)_4N^+$ cation. On iron poisoned by Hg in the presence of La^{3+} the value of $\Delta\eta$ is considerably smaller than that found in the 1 N H_2SO_4 solution without La^{3+} (Fig. 3).

We made attempts to investigate the effect of poisoning iron simultaneously by I^- ions and mercury; however, we did not detect an effect of I^- on the magnitude of the overvoltage lowering at the diffusion of atomic hydrogen to the surface in the case of iron either strongly or weakly poisoned by Hg. For iron strongly poisoned by Hg the absence of such an effect might be explained by the magnitude of the cathodic electrode potential, which is so high that I^- is no longer adsorbed. This explanation is in agreement with the fact that I^- neither has an effect on the magnitude of η on iron strongly poisoned by Hg. But on iron weakly poisoned by Hg the I^- ion raises η and this indicates that it is adsorbed, but on the magnitude of $\Delta\eta$ it has no influence. The reason for such a behavior of I^- in this case is still not clear.

From the reported study it follows that on an iron electrode, when it is poisoned by Hg and I^- ions are present, the relative importance of the electrochemical mechanism of H_{ads} liberation grows in comparison with the catalytic way. It has been proved by direct experiments that, in agreement with the supposition on the effect which the structure of the electric double layer exerts on the discharge of the hydrogen ion, the $(C_4H_9)_4N^+$ and La^{3+} cations, which shift the ψ'-potential to more positive values, retard the electrochemical desorption. The effect which the structure of the electric double layer has on the lowering $\Delta\eta$ of the overvoltage by diffusing hydrogen may be considered as an additional proof that the observed lowering of the overvoltage originates from the electrochemical desorption taking place on the electrode surface.

We seize the opportunity to express our sincere gratitude to Academician A. N. Frumkin for valuable advices in the course of the present study and for a discussion of the results obtained.

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