EFFECT OF SOLUTION pH ON THE ADSORPTION OF IODINE IONS ON A SILVER ELECTRODE

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The halide ions(Cl^-, Br^- and I^-) frequently exert a stimulating effect on the anode dissolution of metals in solutions of electrolytes, which in many cases comes from the metal surfaces being depassivated by the ions. Thus for example B. V. Érshler [1] observed that Cl^- ions have a marked activating effect on the anode dissolution of platinum in acid solutions. Similar observations were made on iron in the work of L. V. Vanyukova and B. N. Kabanov [2], as well as that of Weil and Menzel [3]. In many cases the whole metallic surface does not undergo depassivation, but only a small part of it, and this causes corrosion pitting to develop,which leads to the most dangerous types of corrosion failure in metals.

In the opinion of a number of investigators the effect that we are considering is caused by the halide ions being adsorbed on the metal surface so that they replace the passivating oxygen or OH^- ions located there. An indirect confirmation of this view is given by the experimental observation that the activating effect of the halide ions is reduced when the pH of the solution is increased.

There is very little data in the literature at the present time which tells anything about the effect of pH on the adsorption of anions on metallic surfaces. A qualitative observation of the reduction in anion adsorption when the pH is raised was given by V. E. Kazarinov and N. A. Balashova [4], who were investigating the adsorption of iodine ions on platinum. Along these lines there is also some interest in the work of K. Schwabe [5],who found that the adsorption of various anions on a number of metals is slowed up when adsorbed oxygen is present on the metal surface. A direct determination of the effect of pH on anion adsorption was given in the papers by Hackerman and coworkers [6], where tracer methods were used to show that increasing the pH of the solution causes a reduction in the adsorption of SO_4^{-2} and CrO_4^{-2} ions on iron and steel. Unfortunately the technique used to make the adsorption measurements did not make it possible to find the electrode potentials. Moreover it is well known at the present time that the rate of adsorption of anions and the degree to which they fill the metal surface are markedly dependent on the electrode potential. In particular, this is shown by the data which we obtained during our study of the adsorption of iodine ions on lead and silver electrodes [7-9].

It seemed to be of interest to make a study of the effect of the pH of the solution on the adsorption of halide ions as influenced by the electrode potential of the metal, keeping in mind all the while that the results of the study also make it possible to get closer to an understanding of the mechanism of the corrosion pitting caused by halide ions.

The present paper gives a study of the adsorption of iodine ions on a silver electrode from sulfate solutions (containing KI) over the pH range from 1.9 to 13. The study was made with tracer atoms of the radioactive iodine isotope I^{131}. The method of preparing the electrode surface and the measurement procedure have all been described previously in [7]. Making polarization and radiochemical measurements at the same time made it possible to get a quantitative determination of the adsorption as a function of the pH for different electrode potentials. The degree of filling of the silver surface with iodine ions was found for each pH value as a function of the potential. The potential was kept constant while the adsorption and desorption measurements were being made. At low pH (1.9–4), the quantitative adsorption measurements were made in the range of potentials from -0.5 to + 0.1 v. For values of pH > 6, the measurements were made over a wider potential range (-1.2–+0.1 v). To avoid complications coming from dissolution of the silver and oxidation of the iodine ions the electrode potential was not made more positive than +0.1 v * in any of the experiments.

* The potentials are expressed against a normal hydrogen electrode.

As in the preceding paper [7], the adsorption was from solutions with very low initial halide (KI) concentrations, the salt having been put into the cell before the adsorption measurements were started.

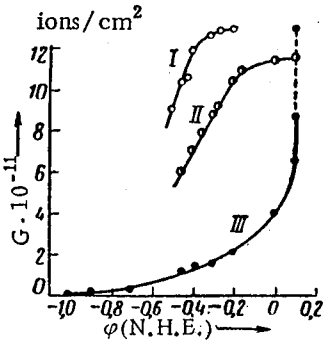

Fig. 1. Adsorption of iodine ions as a function of electrode potential in 0.1 N H_2SO_4 + 0.1 N K_2SO_4 solution containing $1.3 \cdot 10^{-9}$ g-equiv/liter of KI: I) pH 1.9; II) pH 3; III) pH 13.

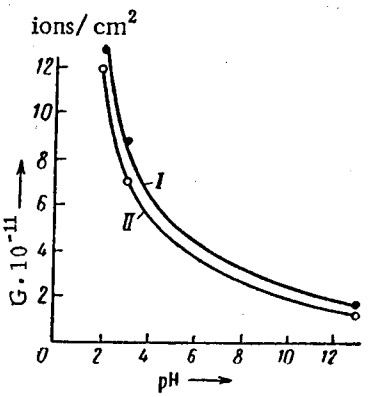

Fig. 2. Adsorption of I^- ions as a function of pH of solution at constant potential: I) $\phi = -0.3$ v; II) $\phi = -0.4$ v.

As with the previous data, the experiments showed principally that in all the solutions studied the adsorption increased markedly as the electrode potential approached positive values, although the effect observed is considerably reduced by going from acid to alkaline solutions (Fig. 1).

It may be seen from the figure that for some particular potential, depending on the pH, the adsorption approached a maximum value. Calculations showed that this corresponded with almost complete (100%) absorption of I^- ions from the solution, which in the present case is an adsorption of $12.7 \cdot 10^{11}$ I^- ions per cm^2 of silver. As may be seen from Fig. 1, the potential at which complete adsorption occurs under these conditions varies considerably with change in pH of the solution. While at pH 1.9 complete adsorption is observed when the potential reaches - 0.325 v, at pH 13 complete adsorption does not occur until the potential is in the vicinity of +0.1 v, and after a longer interval of time than in the first case.

A clearer picture of the effect of the pH of the solution may be obtained from Fig. 2, where each of the curves gives the amount of anion adsorption per cm^2 of electrode surface as a function of pH at constant potential. It follows from the data that increasing the pH always causes a marked reduction in the adsorption. The largest effect is observed in acid solutions (pH < 6), while in alkaline solutions the effect of the pH is considerably less evident. Thus for example increasing the pH from 1.9 to 3 at a potential of -0.3 v reduces the adsorption of iodine ions from $12.55 \cdot 10^{11}$ to $8.8 \cdot 10^{11}$, i.e., it reduces G 1.42 times ($[dG/dpH] \cdot 10^{-11} = 3.4$), while raising the pH from 3 to 13 afterward only reduces the adsorption 5.86 times ($[dG/dpH] \cdot 10^{-11} = 0.72$).

The observed effect of the pH can be explained if we assume that competition occurs between the adsorption of I^- and OH^- ions on the silver surface under our experimental conditions. Here though, increasing the OH^- concentration apparently ought to cause not only a reduction in the adsorption of I^- ions but at the same time a reduction in the strength of the bond between the I^- ions and the adsorbing surface.

TABLE 1. Desorption Rate of Iodine Ions at a Potential of -0.4 v as a Function of the Length of Time the Electrode is Kept at an Adsorption Potential Equal to -0.2 v (pH 1.9)

Time electrode kept at adsorption potential	Number of desorbed ions · 10^{10}				
	5 min	15 min	25 min	40 min	60 min
3.3 hours	3	5	6.2	6.6	8.3
16.0 hours	0.8	2	3	4.5	6.0

To check this latter assumption, some measurements were made in the course of the work on the rate of desorption of iodine ions in solutions with various pH values. It had been found from previous experiments that the desorption rate is to a large extent dependent not only on the adsorption potential (as we have already shown in [7]), but on the length of time the electrode is kept at this potential (Table 1).

It follows from the data given that increasing the length of time the electrode is at the adsorption potential causes a considerable slow up in the desorption of I^- ions afterward at a more negative potential, which shows that the Ag–I^- bond gets stronger with time. These results agree with the qualitative observations made by N. A. Balashova [10] during a study of the adsorption of I^- and Br^- ions on platinum. Keeping in mind what had been observed, the desorption experiments were made in such a way that at the start the electrode was kept for a definite time (several hours) at a fixed potential (adsorption potential), which in any given case would produce almost complete adsorption of the iodine ions from the solution. By using a procedure of this sort before the desorption was started, both the potential of the silver and the degree of filling of the silver surface with adsorbed ions were kept practically the same in all cases. During desorption, the electrode potential was changed 0.5 v in the negative direction, and a record was taken of the increase in concentration of iodine ions in the solution.

The results of one of these experiments are given in Fig. 3, where the time in minutes is plotted as abscissa, and the ordinate is the number of iodine ions adsorbed per cm^2 of the electrode surface. It may be seen from the data given that changing from acid to alkaline solution produces a very large increase in the desorption rate. Thus, for example, in the first five minutes at pH 13 forty-six times as many iodine ions are desorbed from the electrode surface as at pH 1.9. This result shows beyond any doubt that the Ag–I^- adsorption bond gets weaker as the pH of the solution is increased, and explains why the aggressive action of halide ions and in particular of I^- ions is weaker in alkaline solutions than in acid solutions.

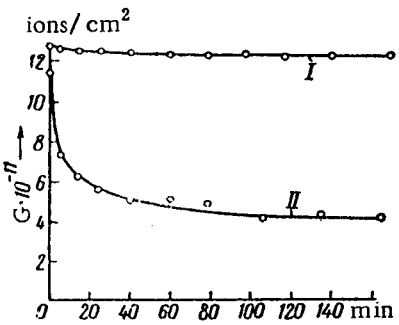

Fig. 3. Change in the number of adsorbed iodine ions during desorption (ϕ_{ads} = + 0.1 v; φ_{des} = - 0.4 v). I) pH 1.9; II) pH 13.

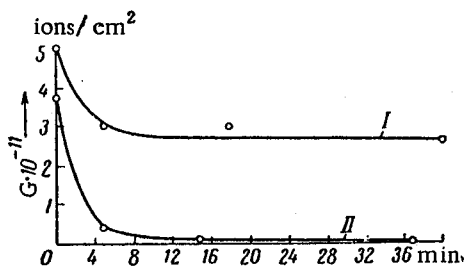

Fig. 4. Desorption rate of I^- ions at various desorption potentials in 1.0 N K_2SO_4 solution containing $0.7 \cdot 10^{-9}$ g-equiv/liter KI (pH 12; ϕ_{ads} = +0.1 v). I) φ_{des} =0.423 v; II) φ_{des} = - 1.246 v.

The small desorption rate could also be explained in terms of slow diffusion of I^- ions from the inside of the crystal lattice of the metal into the solution (if it is assumed that the I^- ions penetrate into the inside of the crystal lattice), but if we keep in mind the small degree of filling of the silver surface with adsorbed ions (equal in the present case to 0.25 % of a monolayer), it is not highly probable that they penetrate into the metal lattice. An indirect confirmation of this is given by the fact that there is only a very weak dependence of the desorption rate on the electrode potential. It may be seen from Fig. 4 that while only a part of the previously adsorbed I^- ions is desorbed at a potential of -0.423 v, very rapid and complete desorption is observed at the more negative potential of -1.246 v.

The increase in the strength of the bond between the adsorbed iodine ions and the surface atoms of the silver observed in our experiments is in accord with the data existing on the increase in the aggressive action of I^- ions produced when the electrode potential is shifted in the positive direction.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
