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Abstract

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

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Halide ions (Cl^-, Br^-, J^-) quite often exert a stimulating influence on the process of anodic dissolution of metals in electrolyte solutions, which in many cases is associated with depassivation of metallic surfaces by these ions. Thus, for example, B. V. Ershler ([1]) observed a strong activating effect of Cl^- ions on the anodic dissolution of platinum in acidic solutions. For iron, analogous observations were made in the works of L. V. Banyukova and B. N. Kabanov ([2]), as well as of Weil and Menzel ([3]). In many cases, depassivation affects not the entire surface of the metal, but only a small part of it, which causes the development of pitting corrosion, leading to the most dangerous types of corrosive destruction of metals.

In the opinion of a number of investigators, the influence of halide ions under consideration is due to their adsorption on the metal surface and the displacement from it of passivating oxygen or OH^- ions. Indirect confirmation of the correctness of this view is the experimentally observed decrease in the activating action of halide ions with increasing pH of the solution.

At present there are few data in the literature characterizing the influence of pH on the adsorption of anions on metallic surfaces. A qualitative observation of a decrease in anion adsorption with increasing pH was made in the work of V. E. Kazarinov and N. A. Balashova ([4]) in a study of the adsorption of iodine ions on platinum. Of some interest in this connection is also the work of K. Schwabe ([5]), in which a slowing of the adsorption of various anions on a number of metals was established in the presence of adsorbed oxygen on the metallic surface. A direct determination of the influence of pH on anion adsorption was made in the works of Hackerman and co-workers ([6]), in which, by means of the radioactive tracer method, it was shown that an increase in the pH of the solution leads to a decrease in the adsorption of SO_4^{2-} and CrO_4^{2-} ions on iron and steel. Unfortunately, the method of adsorption measurements used in these works did not make it possible to determine electrode potentials. Meanwhile, it is now well known that the rate of adsorption of anions and the degree to which they cover the metallic surface depend substantially on the electrode potential. This is indicated, in particular, by the data obtained by us in studying the adsorption of iodine ions on lead and silver electrodes ([7–9]).

Fig. 1. Dependence of the adsorption of iodine ions on the electrode potential in a solution of 0.1 N H_2SO_4 + 0.1 N K_2SO_4 containing 1.3 $\cdot 10^{-9}$ g-equiv/l KJ: I –pH 1.9; II –pH 3; III –pH 13

Figure 1: Fig. 1. Dependence of the adsorption of iodine ions on the electrode potential in a solution of 0.1 N H_2SO_4 + 0.1 N K_2SO_4 containing 1.3 $\cdot 10^{-9}$ g-equiv/l KJ: I –pH 1.9; II –pH 3; III –pH 13

Fig. 2. Dependence of adsorption of J^- ions on the pH of the solution at constant potential: I $-\phi = -0.3$ V; II $-\phi = -0.4$ V

Figure 2: Fig. 2. Dependence of adsorption of J^- ions on the pH of the solution at constant potential: I $-\phi = -0.3$ V; II $-\phi = -0.4$ V

It seemed of interest to investigate the influence of solution pH on the adsorption of halide ions with allowance for the electrode potential of the metal, bearing in mind that the results of such a study also make it possible to approach more closely an understanding of the mechanism of pitting corrosion caused by halide ions.

In the present work, the adsorption of iodine ions on a silver electrode from sulfate solutions (containing additions of KJ) was studied in the pH range from 1.9 to 13. The investigation was carried out by means of the radioactive tracer method using the radioactive isotope of iodine J^{131}. Preparation

the electrode surface, as well as the measurement procedure, were carried out according to the previously described method (7). The method used, involving the simultaneous performance of polarization and radiochemical measurements, makes it possible to carry out a quantitative determination of the adsorption as a function of pH at various electrode potentials. Thus, for each given pH, the degree of coverage of the silver surface by iodine ions was determined as a function of potential. In carrying out adsorption and desorption measurements, the potential was kept constant. For low pH values (1.9–4), the quantitative determination of adsorption was carried out in the potential interval from −0.5 to +0.1 V. For pH values > 6, measurements were carried out over a broader interval of potentials (−1.2 to +0.1 V). In order to avoid complications associated with dissolution of silver and oxidation of iodine ions, the electrode potential in all experiments was not shifted more positive than +0.1 V*.

Fig. 1. Dependence of the adsorption of iodine ions on the electrode potential in a solution of 0.1 N H_2SO_4 + 0.1 N K_2SO_4, containing $1.3 \cdot 10^{-9}$ g-equiv/l KJ:
I –pH 1.9; II –pH 3; III –pH 13

Fig. 2. Dependence of adsorption of J^- ions on the pH of the solution at constant potential: I $-\varphi = -0.3$ V; II $-\varphi = -0.4$ V

As in the preceding work (7), adsorption was carried out from solutions with

very low initial concentrations of the halide salt (KJ), which was introduced into the cell before the start of the adsorption measurements.

In accordance with previously obtained data, the experiments carried out showed first of all that in all the solutions studied the magnitude of adsorption increased noticeably as the electrode potential was shifted toward positive values; however, the effect observed in this case decreased markedly on passing from acidic to alkaline solutions (Fig. 1).

It is evident from the figure presented that, upon reaching a certain potential depending on pH, the magnitude of adsorption reached a limiting value. Calculations showed that in this case there was almost complete (100%) uptake of J^- ions from the solution, which in our case corresponds to adsorption on 1 cm^2 of silver of $12.7 \cdot 10^{11}$ J^- ions. As can be seen from Fig. 1, the potential corresponding, under the conditions of our experiments, to complete adsorption changes markedly with changing pH of the solution; whereas at pH 1.9 complete adsorption was observed upon reaching a potential of −0.325 V, at pH 13 such a state could be attained only at a potential close to +0.1 V, and over a longer period of time than in the first case.

A clearer idea of the influence of the pH of the solution can be obtained from consideration of Fig. 2, where each of the curves shown characterizes—

* Potentials are expressed relative to the normal hydrogen electrode.

characterizes the dependence of the amount of adsorbed anions (per 1 cm^2 of electrode surface) at constant potential on pH. As follows from the data presented, an increase in pH is accompanied in each case by a noticeable decrease in the magnitude of adsorption; moreover, the most significant effect is observed in acidic solutions (pH < 6), whereas in alkaline solutions the influence of pH is manifested much more weakly. Thus, for example, an increase in pH from 1.9 to 3 leads to a decrease in the amount of adsorbed iodide ions at a potential of −0.3 V from $12.55 \cdot 10^{11}$ to $8.8 \cdot 10^{11}$, i.e., by a factor of 1.42 ($|d\Gamma/d\text{pH}| \cdot 10^{-11} = 3.4$), whereas a further increase in pH from 3 to 13 leads to a decrease in the adsorption value by only a factor of 5.86 ($|d\Gamma/d\text{pH}| \cdot 10^{-11} = 0.72$).

The observed influence of pH can be explained if it is assumed that, under the conditions of our experiments, competitive adsorption of J^- and OH^- ions occurred on the silver surface. In this case, however, an increase in the concentration of OH^- should apparently lead not only to a decrease in the adsorption of J^- ions, but also to a decrease in the strength of the bond of these ions with the adsorbing surface.

Table 1

Rate of desorption of iodide ions at a potential of −0.4 V as a function of the duration of holding the electrode at the adsorption potential equal to −0.2 V (pH 1.9)

Time of holding the electrode at the adsorption potential	Amount of desorbed ions $\cdot 10^{-10}$, 5 min	Amount of desorbed ions $\cdot 10^{-10}$, 15 min	Amount of desorbed ions $\cdot 10^{-10}$, 25 min	Amount of desorbed ions $\cdot 10^{-10}$, 40 min	Amount of desorbed ions $\cdot 10^{-10}$, 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 verify this latter assumption, the rate of desorption of iodide ions was measured in solutions with different pH values. Preliminary experiments established that the rate of desorption depends substantially not only on the adsorption potential (as was shown by us earlier ([7])), but also on the duration of holding the electrode at this potential (Table 1).

From the data presented it follows that an increase in the time during which the electrode remains at the adsorption potential is accompanied by a significant slowing of the subsequent desorption rate of J^- ions at a more negative potential, which indicates strengthening of the Ag—J^- bond with time. These results agree with the qualitative observations made by N. A. Balashova ([10]) in studying the adsorption of J^- and Br^- ions on platinum. Taking this dependence into account, the desorption experiments were carried out in such a way that first the electrode was held for a definite time (several hours) at a specified potential value (the adsorption potential), which in every case corresponded to almost complete adsorption of iodide ions from the solution. With this procedure, before the start of desorption not only the magnitude of the silver potential but also the degree of filling of its surface by adsorbed ions remained practically the same in all cases. During desorption, the electrode potential was shifted toward negative values by 0.5 V, and the increase in the concentration of iodide ions in the solution was recorded.

The results of one such experiment are shown in Fig. 3, where the abscissa gives time in minutes and the ordinate gives the amount of iodide ions adsorbed per 1 cm^2 of electrode surface. From the data presented it is evident that the transition from an acidic to an alkaline solution is accompanied by a very strong increase in the desorption rate. Thus, for example, during the first 5 minutes at pH 13, 46 times more iodide ions were desorbed from the electrode surface than at pH 1.9. This result undoubtedly indicates a weakening of the strength of the adsorption bond Ag—J^- with increasing pH of the solution and explains why the aggressive action of halide ions and, in particular, of J^- ions in alkaline solutions was manifested more weakly than in acidic solutions.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

The slowness of desorption could also be explained by the slowness of diffusion of J^- ions from the depth of the metal crystal lattice into the solution (if it is assumed that J^- penetrates into the depth of the crystal lattice); however, taking into account the very slight coverage of the silver surface by adsorbed ions (equal in this case to 0.25% of a monolayer), their penetration into the metal lattice is unlikely. An indirect confirmation of this may also be the very strong dependence of the desorption rate on the electrode potential. As is seen from Fig. 4, whereas at a potential of −0.423 V only part

Fig. 3. Change in the amount of adsorbed iodine ions during desorption ($\varphi_{ads} = +0.1$ V; $\varphi_{des} = -0.4$ V); I–pH 1.9; II–pH 13

Fig. 4. Rate of desorption of J^- ions at different desorption potentials in a 1.0 N K_2SO_4 solution containing $0.7 \cdot 10^{-9}$ g-equiv/L KJ (pH 12; $\varphi_{ads} = +0.1$ V). I–$\varphi_{des} = -0.423$ V; II–$\varphi_{des} = -1.246$ V

of the previously adsorbed J^- ions is desorbed, at a more negative potential, equal to −1.246 V, very rapid and complete desorption is observed.

The increase in the strength of the bond between the adsorbed iodine ions and the surface silver atoms observed in our experiments is consistent with the available data on the increase in the aggressive action of these anions when the electrode potential is shifted toward positive values.

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