SPECIFIC ADSORPTION OF IODINE IONS ON SILVER

![Fig. 1](image)

1961

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

Ya. M. Kolotyrkin and L. A. Medvedeva

SPECIFIC ADSORPTION OF IODINE IONS ON SILVER

(Presented by Academician V. A. Kargin on 2 February 1961)

In order to verify the correctness of conclusions drawn earlier (^{1,2}) concerning the mechanism by which adsorbing anions affect the kinetics of electrode reactions, the present work investigated the specific adsorption of iodine ions on silver and the influence of this adsorption on the hydrogen overvoltage on this metal in $1.0\,N$ H_2SO_4. The magnitude of the adsorption was determined quantitatively by a radiochemical method, using the radioisotope J^{131} as the labeled atom. The adsorption value was determined from the change in the activity of the solution. The method and the basic procedure of the radiochemical and polarization measurements, carried out in one and the same apparatus, are described in the preceding article (^{1}).

Fig. 1. Dependence of the adsorption value of J^- ions on the electrode potential in a solution of $1.0\,N$ H_2SO_4 containing $1 \cdot 10^{-7}$ g-equiv/l KJ.

The great affinity of silver for iodine ions made it possible to carry out the studies with smooth electrodes having an apparent surface area of 10 cm^2. The concentration of J^- in the solution was varied from $1 \cdot 10^{-9}$ to $1 \cdot 10^{-5}$ g-equiv/l. When working with small concentrations ($< 1 \cdot 10^{-7}$ g-equiv/l), only one active isotope, J^{131}, was introduced into the solution. The volume of solution from which the adsorption was determined ranged in different experiments from 25 to 50 cm^3.

Before the experiment, the surface of the electrodes was cleaned with a very fine fraction of glass powder and thoroughly washed with twice-distilled water. The true surface area of the electrodes was determined from the value of the capacitance of the electrical double layer, which in turn was measured by means of the method described earlier (^{3}). From these measurements it was found that the roughness factor of the electrodes used was close to 3. All measurements were carried out at room temperature in an atmosphere of hydrogen, which was carefully purified of traces of oxygen.

Fig. 2

Figure 2: Fig. 2

The experiments were carried out in such a way that, at each specified value of the potential, the electrode was held for a time sufficient to establish adsorption equilibrium in the system. This made it possible to determine the value of the stationary surface coverage at various potentials, as well as the dependence of this value on the KJ concentration in the initial solution at one and the same potential. Comparison of the data obtained with the results of polarization measurements made it possible to establish a relationship between the degree of coverage of the electrode surface by adsorbed J^- and the change in the hydrogen overvoltage caused by adsorption of iodine ions.

To assess the state of the silver surface in the presence of adsorbed J^- ions, the differential capacitance of the electrical double layer of this metal was measured over a wide range of potentials, and also the···

the rate of their desorption as a function of the adsorption and desorption potentials was measured.

As can be seen from Fig. 1, for the comparatively narrow range of potentials investigated, the magnitude of adsorption increases linearly as the potential is shifted toward positive values. Such a linear dependence was observed practically for all investigated KJ concentrations in the initial solution.

For a given constant value of the potential, an increase in the KJ concentration is accompanied by an increase in adsorption; moreover, over a considerable concentration interval from 10^{-9} to 10^{-6} g-equiv/l the dependence between these quantities is close to linear.

Analogously to what was established earlier for lead (^{1}), the adsorption of iodine ions on a silver electrode is completely reversible in the sense that, irrespective of the direction in which the polarization is changed during the measurement, the adsorption value at each given potential remains unchanged. Accordingly, shifting the potential toward negative values is accompanied by partial desorption of J^- ions, and conversely—a shift of the potential toward positive values leads to additional adsorption.

Fig. 2. Kinetics of desorption of iodine ions at $\varphi = -0.335$ V for different adsorption potentials: I—for $\varphi = -0.174$ V, II—for $\varphi = -0.124$ V

Analogously to what was established earlier for iron (^{4}), the adsorption of J^- on silver leads to a fairly considerable (by a factor of 2-3) decrease in the differential capacitance of the electrical double layer, which undoubtedly indicates the presence of a specific interaction between these ions and the surface atoms of the electrode metal.

Fig. 3. Dependence of the hydrogen overvoltage on the logarithm of the current

Fig. 3

Figure 3: Fig. 3

Fig. 4. Dependence between the change in hydrogen overvoltage and the degree of coverage of the silver surface by adsorbed iodine ions

Figure 4: Fig. 4. Dependence between the change in hydrogen overvoltage and the degree of coverage of the silver surface by adsorbed iodine ions

density in $1.0\,N$ H_2SO_4 (1) and in an acid containing $2.6 \cdot 10^{-9}$ g-equiv/l KJ (2)

Judging from the results of desorption measurements, the strength of the adsorption bond in this case does not remain constant, but increases noticeably as the potential is shifted toward positive values. Data presented in Fig. 2 support this conclusion. The corresponding experiments were carried out in such a way that initially the electrode was polarized to a potential at which complete adsorption of iodine ions from the solution occurred. Owing to this circumstance, different adsorption potentials, equal in this case to -0.174 and -0.124 V, corresponded to the same surface coverage, close to $16.9 \cdot 10^{11}$ ions/cm^2. However, despite this, subsequent desorption at one and the same potential, equal to -0.335 V, proceeded the more slowly, the more positive the adsorption potential had been. Thus, for example, for the adsorption potentials indicated above, subsequent desorption of the same quantity of J^-, equal to $3 \cdot 10^{10}$ ions/cm^2, occurred in times equal respectively to 27 and 110 min.

The dependence of the desorption rate on the potential of the preliminary polarization is also indicated by the data presented in Table 1. In these experiments the desorption potential had the value -0.335 V, and the adsorption potentials were -0.145, -0.050, and $+0.100$ V; the initial KJ concentration was equal to $1.2 \cdot 10^{-9}$ g-equiv/l.

All other conditions being equal, the rate of desorption depends substantially

also on the desorption potential. In our experiments it was established that, for one and the same adsorption potential (at one and the same coverage), the desorption rate is the greater, the more negative the potential at which desorption is carried out.

The results of polarization measurements showed that adsorption of iodine ions on silver (in contrast to lead) over a wide range of KJ concentrations from 10^{-9} to 10^{-3} g-equiv/l is accompanied only by an increase in the hydrogen overvoltage.

In Fig. 3 the curves shown characterize the dependence of the rate of hydrogen evolution on the potential in $1.0N$ H_2SO_4 before (curve 1) and after (curve 2) introduction into the solution of KJ in an amount of $2.6 \cdot 10^{-9}$ g-equiv/l.

Fig. 4. Dependence between the change in hydrogen overvoltage and the degree of coverage of the silver surface by adsorbed iodine ions

Because of the slow establishment of adsorption equilibrium in the system, the course of the polarization curve in solutions containing KJ depends substantially on the rate of measurement. This is shown by the data given in Fig. 3, where, in contrast to curve 2, curve $2'$ was obtained by rapid measurement. At the current density corresponding to the position of point a, the electrode was held for a prolonged time; in this case a shift of the potential with time in the negative direction was observed, to the value corresponding to the stationary, i.e., slowly recorded, curve. Simultaneous adsorption measurements showed that such a change in potential is accompanied by an increase in the number of J^- ions adsorbed on the silver surface. Thus, these data made it possible to establish that the experimentally observed decrease in the slope of the hydrogen overvoltage curve is due to an increase in the degree of coverage of the surface by adsorbed ions with a shift of the electrode potential toward positive values. By comparing the results of polarization and adsorption measurements obtained under identical conditions, a curve was constructed (Fig. 4) expressing the dependence of the observed increase in overvoltage on the degree of coverage of the surface by adsorbed iodine ions. It was assumed here that complete filling of the surface corresponds to the adsorption of one J^- ion for each surface silver atom.

Table 1

Number of J^- ions ($\Gamma \cdot 10^{-10}$), adsorbed from 1 cm^2	Time in minutes for various adsorption potentials	Time in minutes for various adsorption potentials	Time in minutes for various adsorption potentials
	−0.145 V	−0.050 V	+0.100 V
1.6	2.5	15	20
2.1	7.5	27.5	45
2.45	12.5	37.5	110

From the data presented it is evident that adsorption of ions in an amount sufficient to form only hundredths of a monolayer leads to noticeable inhibition of the hydrogen-evolution process, which increases regularly as the degree of coverage of the surface by adsorbed particles increases. In accordance with this, the magnitude of the overvoltage at a given current density also increases noticeably with an increase in the concentration of KJ in the solution. Thus, for example, an increase in the KJ concentration from $0.9 \cdot 10^{-9} N$ to $8 \cdot 10^{-7} N$ was accompanied in our case by an increase in the overvoltage (at $\lg i = 1 \cdot 10^{-5}$ A/cm^2) by almost 110 mV. It should be noted, however, that such an increase in overvoltage is observed only until a definite KJ concentration is reached, after which its magnitude ceases to depend on the concentration of this salt in the solution.

For understanding the mechanism of the influence of adsorbed J^- ions on the kinetics of H_2 evolution at a silver electrode, the data obtained in the present work are of interest, from which it follows that intro-

addition of small amounts of KJ ($8 \cdot 10^{-7}$ g-eq/l) to the acid solution leads to a sharp reduction in the length of the hydrogen delay on the charging curve, i.e., is accompanied by a decrease in the amount of hydrogen adsorbed on the surface of the electrode metal.

This result is direct confirmation of the previously advanced assumption (^{1,2}), according to which the specific adsorption of halide ions on the surface of an electrode metal is accompanied not only by a change in the structure of the electrical double layer at the metal—solution boundary, but also by a change in the catalytic properties of the surface, manifested in a decrease in the adsorption energy of hydrogen, which naturally should lead to an increase in the activation energy of the discharge process of hydrogen ions and, consequently, to an increase in overvoltage.

The observed difference in the nature of the influence of adsorbed J^- ions on the kinetics of H_2 evolution on silver and lead electrodes is undoubtedly associated with the higher adsorptive capacity of silver with respect to hydrogen; because of this, the effects connected with poisoning of the electrode surface by adsorbed anions appear more strongly in this case and exceed in magnitude the effects connected with the change in the structure of the double layer.

Physical-Chemical Institute
named after L. Ya. Karpov

Received
1 II 1961

REFERENCES

1. L. A. Medvedeva, Ya. M. Kolotyrkin, ZhFKh, **31**, 2668 (1957).
2. J. M. Kolotyrkin, Trans. Farad. Soc., **55**, 455 (1959).
3. T. I. Borisova, B. V. Ershler, A. I. Frumkin, ZhFKh, **22**, 925 (1948).
4. V. V. Losev, DAN, **88**, 3, 499 (1953).

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