INFLUENCE OF THE ADSORPTION ON IODIDE ON THE CATHODIC LIBERATION OF HYDROGEN FROM ACID SOLUTIONS ON AN IRON ELECTRODE

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It is known that in the electrochemical liberation of hydrogen from acid solutions on iron, the introduction of iodide into the solution increases the overvoltage of the reaction (see, for example [1, 2]). The observed decrease in the reaction rate may reach a value of more than one order of magnitude [2]. The most widespread hypothesis explaining this effect contains the assumption that the adsorption of iodide leads to a decrease in the energy of adsorption of atomic hydrogen as a result of a mutual influence of adsorbed particles. Another explanation is that adsorbed iodide blocks part of the surface. The blocking of a substantial portion of the surface of semicrystalline iron, considering its inhomogeneity, should also lead to a change in the energy of adsorption of atomic hydrogen, which participates in the reaction. Thus, both explanations operate on the assumption of a decrease in the energy of the Me–H bond (E_H) in the presence of iodide in solution.

It is known that the protium–tritium isotopic kinetic effect (IKE) in the electrolytic liberation of hydrogen is sensitive to a change in E_H [3]. In view of this, we were interested in measuring the IKE on iron in acid solutions containing and not containing iodide.

The measurements were performed according to a procedure analogous to that used earlier [4].* In order to exclude the influence of preparation of the electrode, the coefficient of separation of protium and tritium, S, was measured first in 0.5M H_2SO_4 solution at a current density of $2 \cdot 10^{-2}$ A/cm^2, after which potassium iodide with a concentration of 0.4M was introduced into the solution, and S was measured at various current densities. The introduction of iodide shifted the polarization curve by 80-100 mV in the direction of negative values in our case, which was close to the effects observed in [1, 2].

It was discovered that the presence of iodide in solution has no effect on the value of the IKE: in a solution without iodide $S = 18.1 \pm 1$, which agrees with our previous results [5]; in a solution with iodide $S = 18.3 \pm 0.7$.† In the latter case, the measurement was performed in the range of potentials −0.560 to −0.680 V. Just as in pure acid, independence of S from the potential was observed.

If we assume that on iron the kinetics of the liberation of hydrogen, just as on melts of the mercury type, are determined by slow discharging,‡ then we can write:

$$\ln i = \ln K_H + \ln [H_3O^+]^{\alpha} + \frac{\alpha E_H}{RT} + \alpha\eta \frac{F}{RT}. \quad (1)$$

Here K_H, η, E_H, and i are the preexponential factor of the reaction, the overvoltage, the energy of the Me–H bond, and the current, respectively. The remaining notations are as usual. Differentiating Eq. (1) with respect to E_H, we obtain

$$\left(\frac{\partial \eta}{\partial E_H}\right)_i = -\left(\frac{2{,}3RT}{\alpha F} \cdot \frac{\partial \lg K_H}{\partial E_H} + \frac{1}{F}\right). \quad (2)$$

The value $\partial \log K_H / \partial E_H = -0.2$ mole/kcal for cases when the kinetics of the liberation of hydrogen is determined by slow discharging. It was determined from the dependence of $K_H(E_H)$ according to the data of [7, 8]. Knowing

*Vacuum-smelted iron (99.89%) and solutions in double-distilled water were used; "special purity" sulfuric acid was redistilled twice; twice-recrystallized potassium iodide was calcined at 600°C before the experiment.

†Average value from ten measurements.

‡The difficulties arising in the explanation of the data according to the IKE on iron within the framework of this mechanism have already been indicated in our previous communication [6].

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the slope of the Tafel function on iron $2.3\,RT/\alpha F = 120$ mV, we find $(\partial\eta/\partial E_H)_i = -0.018$ V·mole/kcal. Thus, the increase in the overvoltage by 80 mV should be caused by a decrease in E_H by approximately 4.5 kcal/mole if we follow the assumption that the increase in η in the presence of iodine is due to a decrease in E_H. The estimate cited gives only the lower limit of the decrease in E_H, since the adsorption of iodide on the surface should change the ψ'-potential to a greater or lesser degree and increase η, as it occurs on mercury. Therefore, the total decrease in E_H should be greater than 4.5 kcal/mole, so as to compensate for the influence of the ψ'-potential.

A change in E_H of 4.5 kcal/mole is sufficiently large to have a substantial effect on the IKE. Thus, in [3, 7] an influence of E_H on the IKE was detected in measurements on mercury, lead, and thallium amalgam, despite the fact that on these metals the difference in E_H is less than 4.5 kcal/mole [7]. Thus, it can be asserted that the absence of an influence in the adsorption of iodide on iron on the IKE is evidence that the increase in the overvoltage on iron when iodide is added is not associated with a change in E_H. This conclusion was drawn on the assumption that slow discharging is realized on iron. For the other proposed mechanisms of the liberation of hydrogen, we are unable to estimate the values of the change in E_H, and there are no measurements of the IKE on metals on which the existence of these mechanisms has been demonstrated. However, we can draw a purely qualitative conclusion: to the degree that the IKE is insensitive to iodide in solution, to that extent the effects caused by iodide are not associated with the change in the energy of adsorption of atomic hydrogen, since the IKE should depend on this parameter for any mechanism including adsorbed hydrogen as an intermediate product.*

The absence of an influence of iodide on the IKE and its influence on the overvoltage are evidence that the step determining the rate of the process as a whole and the step responsible for the IKE are different steps. This conclusion agrees with the mechanism of the liberation of hydrogen that we proposed in [6]. This process consists of an irreversible chemical reaction of formation of molecular hydrogen from a water molecule on the surface of the metal:

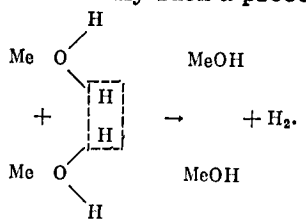
$$2H_2O + 2Me \rightarrow 2MeOH + H_2. \qquad (3)$$

The intrinsically electrochemical step, determining the rate of the process, is a reduction of the metal surface:

$$MeOH + H_3O^+ + e \rightarrow Me + 2H_2O. \qquad (4)$$

In [6] it was shown that this mechanism satisfies the kinetic principles of the liberation of hydrogen observed on iron, in particular, the data on the IKE. There also it is suggested that iodide affects the rate of the cathodic reaction. The adsorption of iodide leads either to a decrease in the number of reactive OH groups on the surface or to an increase in the energy of the Me–OH bond. Both inhibit the step (4), lowering the rate of the reaction as a whole, but do not directly affect the process of formation of a hydrogen molecule, i.e., have no effect on the IKE.

We cannot judge the intermediate steps of the chemical reaction of the metal with water with assurance. However, since the adsorption of iodide does not influence the IKE, we can assert that it does not affect the energy of the hydrogen atoms that form a hydrogen molecule in the course of the reaction. This also pertains to the Me–H bond, if Me–H is an intermediate product of the formation of a hydrogen molecule, as we suggested in [6]. A different situation arises if we assume that reaction (3) is elementary, i.e., proceeds without the formation of intermediate products. Schematically such a process can be represented in the form



(5)

Here the hydrogen molecule is formed in the process of oxidation of two neighboring free metal atoms. In such a scheme the influence of the nature of the metal on the IKE (on iron it is greater than on chromium [5]) is manifested in the distance between adsorption centers. This determines the distance from which the protons in the water molecules pass into the final state in the hydrogen molecule, i.e., determines the probability of such a transition and ultimately the difference in the rates of the reaction in which isotopes of different mass

*An exception is the case with reversible electrochemical desorption, but in the presence of such a step, always $S = 6.2$ [9, 10], which does not correspond to the data obtained on iron.

participate. The adsorption of iodide will change the rate of this reaction on account of a strength of the Me–OH bond; however, it does not affect the isotopic effect, since the distance between adsorption centers is inconstant.

LITERATURE CITED

1. K. E. Heusler and G. H. Cartledge, J. Electrochem. Soc., 108, 732 (1961).
2. Z. A. Iofa and Fan Lyong Kam, Élektrokhimiya, 7, 696 (1971).
3. V. M. Tsionskii and L. I. Krishtalik, Élektrokhimiya, 6, 265 (1970).
4. V. M. Tsionskii and L. I. Krishtalik, Élektrokhimiya, 5, 1184 (1969).
5. T. Sh. Korkashvili, V. M. Tsionskii, and L. I. Krishtalik, Élektrokhimiya, 15, 1383 (1979).
6. V. M. Tsionskii and T. Sh. Korkashvili, Élektrokhimiya, 16, 451 (1980).
7. L. I. Krishtalik and V. M. Tsionski, J. Electroanal. Chem., 31, 363 (1971).
8. V. M. Tsionskii, Élektrokhimiya, 5, 1500 (1969).
9. J. O'M. Bockris and S. Srinivasan, J. Electrochem. Soc., 111, 844 (1964).
10. V. M. Tsionskii, Élektrokhimiya, 11, 1145 (1975).

MECHANISM OF THE FORMATION OF AN ANODIC FILM OF $Fe(OH)_2$ ON IRON IN ALKALINE SOLUTIONS

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During the first anodic process on an iron electrode in solutions of alkali, the basic reaction product is $Fe(OH)_2$, deposited in the form of a film on the electrode [1, 2]. The increase in the film thickness at constant potential obeys a parabolic law, which can be explained by the occurrence of a process of slow nonsteady-state diffusion of Fe^{2+} ions through the film to its boundary with its solution. A consequence of the parabolic law of growth is a direct proportionality of the limiting current of the reaction to the reciprocal of the square root of the time ($i = kt^{-1/2}$). The slope of the i versus $t^{-1/2}$ straight lines characterizes the value of the ionic conductivity of the $Fe(OH)_2$ film formed [3].

In [4] it was suggested that the main factor in the process is the overcoming of the energy barrier by the Fe^{2+} ion under the action of the applied potential and the escape of these ions from the lattice of $Fe(OH)_2$ into the interstices, followed by their movement under the action of the established potential and concentration gradients along the vacancies and defects to the boundary of the film with the solution [5]. From this picture it follows that the presence of additions of certain anions in alkali, as well as an increase in the alkali concentration, lead to adsorption of anions and OH^- ions at the lattice points. The supplementary negative charge created by them, surrounding the Fe^{2+} ion in the lattice, facilitates the escape of the latter into interstices, leading to an increase in the ionic conductivity of the film and the limiting current of the anodic reaction. Additions of Ca^{2+}, Mg^{2+}, and other cations act in the opposite direction, lowering the ionic conductivity of the $Fe(OH)_2$ film.

In this work we studied the influence of temperature on the limiting currents of the formation of $Fe(OH)_2$ on the time at a constant potential of -0.86 V (HgO) on a smooth electrode of zone-melted iron. The electrolytes were freshly prepared solutions of KOH, purified by cathodic polarization on a platinum mesh for 2 h. The salts used for the additives were subjected to double recrystallization. Before the experiment the electrodes were thoroughly freed of oxide films by polishing with fine glass powder, etching in 1N H_2SO_4, and cathodic polarization with a current of 10^{-2} A/cm^2 in the working solution. Thermostatic control of the cell was performed with an accuracy of ± 1°C with an ultrathermostat. The experiements were conducted in an atmosphere of argon. The potentials at various experimental temperatures were measured relative to a mercury oxide reference electrode, with the same KOH concentration as the investigated solution, and kept at a constant temperature of 17°C. The values of the limiting currents on various samples of electrodes under the same conditions might differ substantially; however, on each individual electrode the reproducibility of the experiments at all the investigated temperatures was about 5%.

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