BRIEF COMMUNICATIONS

MECHANISM OF THE ACTION OF I^- IONS ON BISMUTH IONIZATION

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It is known that a decrease in the rate of corrosion or anodic dissolution of metal electrodes of an order of magnitude or more may be observed when an inhibiting component is adsorbed on the electrode in amounts sufficient to form only a few tenths, or even a few hundredths, of a monomolecular layer [1-4].

With the object of elucidating in detail the mechanism by which species adsorbed on electrodes influence the anodic dissolution of metals, it would be of interest to study these processes under the simplest conditions, where there is no competing adsorption of any other species and the possibility of passivation by oxygen adsorption is eliminated. A study of the action of I^- ions on the ionization of bismuth would be of definite interest from this point of view. Indeed, bismuth acts as an ideally polarizable electrode in perchloric acid solutions right up to the start of its anodic dissolution [5], and no significant specific adsorption of ClO_4^- ions occurs on it [6]. The anodic dissolution of bismuth takes place at potentials more positive than ~0.2 V (N.H.E.), which corresponds, to judge from the zero-charge potential of bismuth,* to a high positive charge on the electrode surface, and at which passivation of the electrode is not observed, as follows from the results of a study of the discharge-ionization kinetics of bismuth [8].

We used the radiochemical method of [9, 10], which allows continuous determination of the adsorption of a labeled component of the solution on the electrode at the same time as the rate of the electrode process is being measured. The adsorption measurements were carried out using the radioisotope I^{131}. The experiments were performed under potentiostatic conditions with 1 M $HClO_4$ as supporting electrolyte in an atmosphere of carefully purified argon. All potentials are given relative to the standard hydrogen electrode.

We measured the rate of anodic dissolution of bismuth in 1 M $HClO_4$ at $\varphi = 0.285$ V; this is shown by the horizontal dotted line in Fig. 1. Then, with strong cathodic polarization of the electrode ($\varphi = -0.7$ V), a labeled NaI solution was introduced into the cell until the NaI concentration in solution was $1 \cdot 10^{-7}$ M, and the activity of the solution was measured under conditions where there were no adsorbed I^- ions on the electrode [9]. After this, the potential was reset at $\varphi = 0.285$ V, and we observed simultaneously the increase in I^- adsorption on the electrode and the decrease in the rate of anodic bismuth dissolution up to the point where the rate remained practically constant at $2 \cdot 10^{-5}$ A/cm^2 and the adsorption remained practically constant at $2 \cdot 10^{-10}$ g-ion/cm^2 after a period of approximately 25-30 min (Fig. 1).† It should be noted that although the surface coverage by I^- ions under the steady-state conditions is no more than 18% (see below), the rate of the anodic process was only about one twelfth of that in pure 1 M $HClO_4$. Consequently, the retarding action of the I^- ions cannot be explained on the basis of a simple surface blocking mechanism.

A completely different picture was observed in the case of a solution with an NaI concentration of $1 \cdot 10^{-6}$ M (Fig. 2). The experiment was performed in this case in the same order as described above. After changing the potential from $\varphi = -0.7$ V to $\varphi = 0.285$ V, the amount of I^- adsorbed on the electrode

*The zero-charge potential of bismuth is $\varphi_{zc} = -0.4$ V [7].
†The concentration of NaI in the bulk of the solution had dropped to $2.0 \cdot 10^{-8}$ M at this point.

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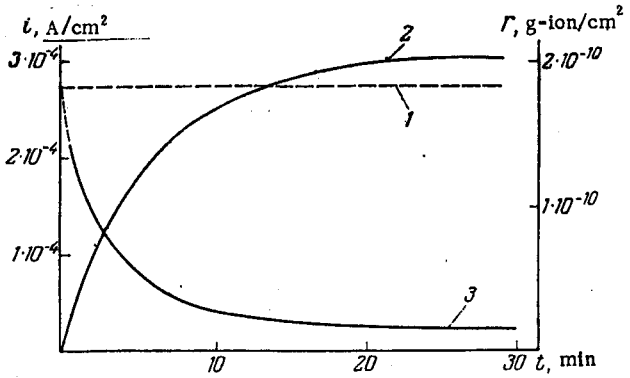

Fig. 1. 1) Rate of bismuth dissolution in 1 M $HClO_4$ at $\varphi = 0.285$ V; 2, 3) variation in the adsorption of I^- ions and the rate of anodic bismuth dissolution with time at the same potential in a solution with an initial NaI concentration of $1 \cdot 10^{-7}$ M.

surface was still observed to increase continuously until a practically constant adsorption value of $1.1 \cdot 10^{-9}$ g-ion/cm²* was established after about 12-15 min, but the curve representing the time dependence of the rate of the anodic process at $\varphi = 0.285$ V was more complex and nonmonotonic. An approximately threefold decrease in the rate of the process is observed first, after which the further increase of the adsorption of I^- ions on the electrode no longer leads to an increase in the retardation of the process but to a gradual increase in its rate; when a practically constant adsorption value is reached,† the rate of the anodic process proves to be even somewhat higher than in the pure acid. When the electrode is then kept at the same potential, the rate of the anodic process again decreases somewhat with time, while the I^- ion adsorption on the electrode remains almost constant.

In an analogous experiment with a $1 \cdot 10^{-5}$ M NaI solution, the rate minimum of the anodic process is very shallow and the steady-state process rate at $\varphi = 0.285$ V is several times higher than the rate of bismuth dissolution in 1 M $HClO_4$.

Thus, iodide ions strongly retard the anodic process at low degrees of surface coverage, whereas their retarding action changes to an accelerating action at higher coverages. How can we explain this peculiar action of I^- ions on the bismuth ionization process?

The observed strong retarding action of the I^- ions in the $1 \cdot 10^{-7}$ M NaI solution (a more than 10-fold decrease in the rate of the process at a surface coverage of less than 18%) is analogous to the previously

*As an approximate calculation showed, this value is less than monolayer coverage. Hence, it follows that the coverage reached in the $1 \cdot 10^{-7}$ M NaI solution (Fig. 1) is, in any case, not more than 18% of the monolayer coverage.

†The bulk concentration of NaI at this point was $6.5 \cdot 10^{-7}$ M.

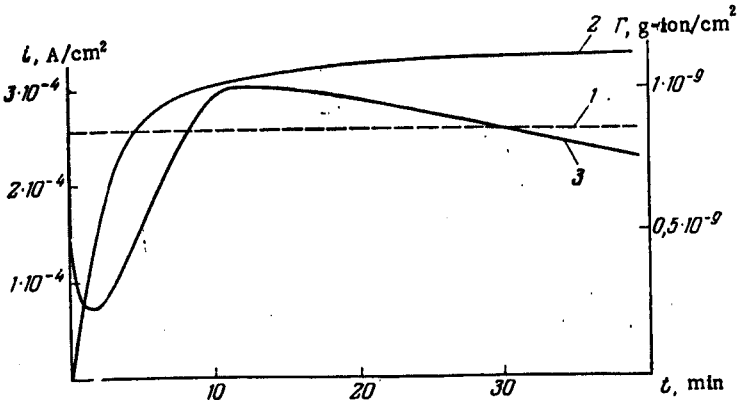

Fig. 2. The same curves as in Fig. 1 but with an initial NaI concentration of $1 \cdot 10^{-6}$ M.

observed action of I^- ions on the anodic dissolution of nickel [3, 4], and may be explained, as in [4], on the basis of the concept of nonuniformity of the electrode surface.* For this, we must assume the presence of active centers on the surface, the dissolution of which centers makes the major contribution to the total rate of the anodic process, it being precisely these centers that are primarily covered by the adsorbed inhibitor species. It is this that leads to such a sharp decrease in the overall rate of the anodic process.

The unusual minimum in the curve representing the dependence of the rate of the anodic process on time (Fig. 2), and consequently on the degree of I^- adsorption on the electrode, observed in the more concentrated NaI solution is obviously of particular interest. We can explain this minimum if we assume that the I^- ions adsorbed on the bismuth can have both a retarding and an accelerating effect on the anodic dissolution of bismuth, depending on the type of surface centers on which they are adsorbed. In the initial period, the centers with the strongest bonding are covered preferentially by the I^- ions, which leads to retardation of the anodic process. As these centers become covered, the coverage of centers with weaker bonding, on which the I^- ions have no longer a retarding but an accelerating action on the anodic process, takes place. As a result, the further increase in the degree of coverage leads to gradual acceleration of the anodic process.

On the basis of the concept that the bismuth surface is nonuniform and that the action of the I^- ions is different when they are adsorbed on centers with different bond energies, we can also explain another effect which is incomprehensible at first glance. As can be seen from a comparison of Figs. 1 and 2, at one and the same surface coverage (and constant potential) I^- ions adsorbed from solutions with different NaI concentrations have a substantially different retarding action on the anodic process. Thus, after adsorptive equilibrium has been reached ($2.0 \cdot 10^{-10}$ g-ion/cm^2) and a constant rate of bismuth dissolution has been established in $1 \cdot 10^{-7}$ M NaI solution, we observe a 12-fold decrease in the rate of the process (Fig. 1), whereas in the case of adsorption from a more concentrated NaI solution the anodic process is retarded by a factor of only three when the same (nonequilibrium in this case) adsorption value is reached, i.e., the degree of retardation in this case is one quarter of that in the more dilute NaI solution at the same surface coverage. To explain this effect, we must take into account not only the character of the bond energy distribution of the adsorbed species under equilibrium conditions, but also the kinetics of the adsorption of I^- ions on the regularly nonuniform surface of the bismuth electrode [9, 10]. Whereas in the first case, owing to the establishment of adsorptive equilibrium, the I^- ions are adsorbed preferentially on the centers with the strongest bonding and have mainly a retarding effect on the anodic process, in the second case, at the same coverage, adsorptive equilibrium has not yet been established on the electrode and the I^- ions are adsorbed on centers with both strong and weaker bonding, where they have an accelerating effect on the electrode process. As a result, weaker overall retardation of the process is observed at one and the same surface coverage. It should be stressed that this difference in the retarding action of the adsorbed I^- ions at one and the same surface coverage cannot be explained without taking into account the biographic nonuniformity of the electrode surface.

The above concepts also enable us to explain the slight decrease in the rate of the anodic process with time observed after reaching a constant adsorption value (Fig. 2). This effect is probably due to a further redistribution of the I^- ions from the centers with the weaker bonding to the centers with the stronger bonding.†

Thus, I^- ions can have both a retarding and an accelerating effect on the anodic dissolution of bismuth, the character of their action depending on the strength of their bond with the corresponding surface centers. On centers on which the iodine forms a strong bond with the bismuth, approximating to the bond in the individual chemical compound, the adsorbed iodine evidently undergoes substantial dehydration and, to a great extent, gives up its bond with the solution and has a retarding action. The I^- ions adsorbed on centers with weaker bonding facilitate the anodic dissolution of the bismuth by directly participating in the elementary act of charge transfer, in the same way as is observed on bismuth amalgam electrodes [13].

*The concept of surface nonuniformity is perfectly well-founded in the present case, since the surface of bismuth electrodes in the same potential range has already been found to be nonuniform on the basis of adsorption measurements [9, 10].

†The strengthening of the binding of adsorbed anions with time observed in [11, 12] may evidently serve as indirect confirmation of the possibility of such a redistribution of adsorbed species over the electrode surface while the adsorption value remains unchanged.

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