V. V. Losev and A. I. Molodov

1960

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Abstract

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V. V. Losev and A. I. Molodov

The Influence of Anions on the Anodic Dissolution of Indium Amalgam

(Presented by Academician V. A. Kargin, 16 VI 1959)

The rate of the processes of anodic dissolution and electrodeposition of metals depends strongly on the nature of the anions present in the solution. Halide ions noticeably accelerate the cathodic and anodic processes on amalgams of zinc, tin, bismuth, and indium (^1), and also sharply increase the exchange current between amalgams of zinc and bismuth and solutions of their salts (^2). By measuring the exchange current of zinc and cadmium amalgams it was shown that, in the case of solutions containing complexes of metals with anions, anions participate directly in the limiting stage of the electrode process (^3, ^4). The rate of anodic dissolution of cadmium in sulfuric acid is greatly increased in the presence of bromide ions and especially iodide ions (^5). The rate of the anodic dissolution process of platinum in sulfuric acid at constant potential is proportional to the concentration of Cl^- ions in the solution (^6). The mechanism of the accelerating influence of anions on the anodic dissolution of metals has not yet been clarified. Solving this question by ordinary stationary polarization measurements is difficult, since usually, at an appreciable deviation from the equilibrium potential, the polarization is mainly concentration polarization, while the results of polarization measurements near equilibrium cannot be used because of the simultaneous occurrence of the corresponding reverse process. Under certain conditions the latter difficulty can be eliminated. By combining ordinary polarization measurements with radiochemical measurements, one can isolate one of the coupled electrode processes—for example, the anodic one—and study its regularities in the region of the equilibrium potential and even under conditions where the reverse process predominates.

Using this method, with certain improvements (^{7}-10), we studied the influence of the concentration of sodium halides and sulfate on the rate of the true anodic process i_a of dissolution of 0.1 M indium amalgam in a solution of 0.01 M $In(ClO_4)_3$ + 0.01 M $HClO_4$ at various potentials and, in particular, at the equilibrium potential (exchange current).* The experiments were carried out at 20° at a constant ionic strength (3 M), which was maintained by additions of $NaClO_4$. In addition, the dependence of the equilibrium potential of the amalgam on the concentration of halide and sulfate ions was studied.

Figure 1 shows the dependence, found by radiochemical measurements, of the rate of the true anodic process i_a, in A/cm^2, on the potential of the indium amalgam, together with the ordinary polarization curves recorded by current. As can be seen, the process of ionization of indium proceeds at a noticeable

Fig. 1

Figure 1: Fig. 1

rate even under strong cathodic polarization. Figures 2 and 3 present curves obtained by the radiochemical method for the dependence of i_a on the potential at various concentrations of Na_2SO_4 (0.05-0.9 M), NaCl (0.05-2.7 M), NaBr ($1 \cdot 10^{-3}$–2.7 M), and NaJ ($1 \cdot 10^{-3}$–1 M). As can be seen, a linear dependence is observed between φ and $\lg i_a$, while the slope coefficient of the anodic curve b_a does not depend on the concentration of the additives,** therefore sometimes

We did not record complete anodic curves, but confined ourselves to measuring the exchange current (the points in Figs. 2 and 3); in doing so, the straight lines were drawn through the points corresponding to the exchange-current values with the corresponding slope coefficients*.

It follows from Fig. 2 that, with increasing concentration of SO_4^{2-} and Cl^- ions, the anodic curves shift in the negative direction, i.e., the rate of the anodic process increases. To evaluate the dependence of the rate of the true anodic process i_a on the concentration C of these additives at constant potential, a dashed straight line was drawn in Fig. 2 at $\varphi = -0.330$ V; the points of intersection of the anodic curves with this straight line represent the desired values of i_a. If these experimental data are expressed in the form of the equation $i_a = kC^x$, then at low concentrations of Na_2SO_4 (up to $0.2M$) the value of x is close to 1, whereas at higher Na_2SO_4 contents the value of x is not constant and gradually increases with increasing C. At NaCl concentrations below $0.5M$, the value of x in this equation is also not constant and increases approximately from 1.0 to 2.0 with increasing C; in the interval $C = 0.5$–$2.7M$, $x = 2.9$. Apparently, these results indicate the direct participation of SO_4^{2-} and Cl^- ions in the anodic process, and the composition of the complex indium ions formed in the elementary electrochemical act changes with increasing concentration of these ions.

Fig. 1. Polarization curves for In amalgam ($0.1M$) in a solution of $0.01M$ $In(ClO_4)_3$ + $0.1M$ $HClO_4$; **1**–ordinary polarization curves; **2**–true

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* The choice of indium is due to the fact that, in the absence of activating anions, the exchange current of indium amalgam is relatively low (ˆ10). At the same time, it is known from polarographic data ($^{11-}$15) that, during the discharge of indium ions in the presence of halide ions, the half-wave potential shifts strongly to the positive side and the electrode process becomes more reversible.

** b is 0.026-0.027 V for solutions with additions of Na_2SO_4 and 0.025 V for solutions with additions of NaCl and other halides. Consequently, in the absence of halide ions the transfer coefficient for the anodic process β is equal to $2.3RT/b_a = 2.32$ (assuming $\alpha + \beta = 3$) (ˆ9).

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

anodic curve, obtained by the radiochemical method

Fig. 2. Dependence of i_a on potential for a solution of $0.01M$ $In(ClO_4)_3$ + $0.01M$ $HClO_4$ with additives. **a**–Na_2SO_4: **1**–$0.05M$, **2**–$0.1M$, **3**–$0.2M$, **4** –$0.3M$, **5**–$0.6M$, **6**–$0.9M$; **b**–NaCl: **1**–0, **2**–$0.05M$, **3**–$0.1M$, **4**–$0.2M$, **5**–$0.3M$, **6**–$0.5M$, **7**–$0.76M$, **8**–$1.0M$, **9**–$2.0M$, **10**–$2.7M$; black points–exchange current

At high NaCl concentrations, particles of $InCl_3$ probably participate in the electrode process, whereas in solution (judging from the character of the dependence of the equilibrium potential of the amalgam on C) $InCl_2^+$ ions predominate.

In the case of NaBr and NaJ additives (Fig. 3), with increasing concentration of halide ions, not only a shift of the anodic curves is observed, but also a noticeable

* At high concentrations of NaBr and NaJ, the exchange currents are so high that the complete anodic curve cannot be recorded because concentration polarization sets in, and it is necessary to confine oneself to exchange-current measurements. In this case the values of b_a were determined by measuring the exchange current at different concentrations of indium ions in solution (for example, point A in Fig. 3a).

increase in the exchange current. For a quantitative assessment of this accelerating action, Fig. 4 presents the dependences of i_a on the concentrations of NaBr and NaJ at a constant potential ($\varphi = -0.276$ V), obtained from Fig. 3 by the method described above. In the case of NaBr additions the dependence $\lg i_a$ on $\lg C$ is linear in the interval $C = 0.05$–2 M, and the slope of the straight line ($\lg i_a, \lg C$)

Fig. 3. Dependence of i on the potential for a solution of 0.01 M $In(ClO_4)_3$ + 0.01 M $HClO_4$ with additions.
a–NaBr: 1—0; 2—$1{\cdot}10^{-3}$ M; 3—$5{\cdot}10^{-3}$ M; 4—0.01 M; 5—0.02 M; 6—0.05 M; 7—0.1 M; 8—0.2 M; 9—0.5
b–NaJ: 1—0; 2—$1{\cdot}10^{-3}$ M; 3—$2{\cdot}10^{-3}$ M; 4—$5{\cdot}10^{-3}$ M; 5—0.02 M; 6—0.05 M; 7—0.1 M; 8—0.3 M; 9—0.5
black points–exchange current.

is equal to 1.8, i.e., our experimental data can be expressed by the equation $i_a = kC^{1.8}$. It may be assumed that, under these conditions, two Br^- ions participate in the anodic process and $InBr_2^+$ ions are formed, which are in equilibrium with $InBr^{2+}$ ions (the latter predominate in solution up to $C \sim 0.2$ M, while at $C > 0.5$ M indium is present in solution predominantly in the form $InBr_2^+$).

Fig. 4

Figure 4: Fig. 4

This conclusion is consistent with the results of analysis of the dependence of the rate of the true cathodic process i_k on the NaBr concentration (dashed curve in Fig. 4)*. At high NaBr concentrations i_k is practically independent of C, as should be expected for discharge of InBr_2^+ particles, which predominate in solution under these conditions.

In the presence of additions of J^- ions, the slope of the curve $(\lg i_a, \lg C)$ in Fig. 4 is equal to 1.0 over a wide range of C ($2 \cdot 10^{-3}$–$0.2\ M$), i.e., the rate of the true anodic process is directly proportional to the NaJ concentration. Such a dependence can be explained by assuming the direct participation of J^- ions in the anodic process:

$$\mathrm{In} + \mathrm{J}^- \rightleftarrows \mathrm{InJ}^{2+} + 3e.$$

Judging from the character of the dependence of the equilibrium potential of the amalgam on the NaJ concentration, at $C < 0.03\ M$ the In^{3+} ions predominate in solution; they are in equilibrium with InJ^{2+} ions; therefore the concentration of the latter is proportional to the concentration of J^- ions, and the rate of the true cathodic process i_k, like i_a, depends linearly on C.

Fig. 4. Dependence of i_a on the concentrations of NaBr (a) and NaJ (b) at a constant potential ($\varphi = -0.276$ V); dashed lines—the corresponding dependences for i_k.

At higher C, the solution is dominated by InJ^{2+} ions; their concentration changes little with increasing concentration of J^- ions, and therefore i_k is practically independent of C (dotted line in Fig. 4). The results of studying the temperature dependence of the exchange current (in the interval 1—45°) show that the introduction of an NaJ additive ($0.05\,M$) leads to a decrease in the activation energy of the electrode process from 13.4 kcal (^{10}) to 4.5 kcal.

Taking into account the observed dependence of i_a on φ, as well as the linear dependence of i_a on the concentration of the amalgam (^{10}), our experimental data can be expressed by the equation: $i_a = k[\mathrm{In}][\mathrm{J}^-]\exp(\beta\varphi F/RT)$, where $\beta = 2.32$. Similar equations express the rate of the anodic process in the presence

* For an approximate estimate of i_k, one may determine the slope coefficient of the cathodic curve b_k by means of the relation $b_k = 2.3RT/\alpha F$; using the previously found value $\beta = 2.32$ and taking into account the condition $\alpha + \beta = 3$, we obtain $b_k = 0.085$ V. If straight lines with this slope, corresponding to the true cathodic process, are drawn in Fig. 3a through the exchange-current values, and the quantities i_k at constant potential ($\varphi = -0.276$ V) are found, the curve $(\lg i_k, \lg C)$ can be constructed.

of Br^- and Cl^- ions (at high NaCl concentrations), with the difference that i_a will be proportional, respectively, to $[Br^-]^2$ and $[Cl^-]^3$.

As has already been noted (16), there is a well-known parallelism between the accelerating effect of halide anions on electrode processes involving cations and their catalytic action on processes of isotope exchange between cations (17,18) and on other ionic reactions between cations (19,20). Apparently, the mechanism of the influence of halide and certain other anions is similar in both cases: the anions serve as a kind of "bridge" or electron transmitter between cations or, respectively, between a cation and the electrode surface (1,17).

It should be noted that the accelerating action of J^- ions, and also of Br^-, can in general be explained by a change in the structure of the electrical double layer under the influence of their adsorption and by the appearance of a negative ψ_1-potential, which should lead to acceleration of the anodic and cathodic processes (21). This is supported by the fact that strongly adsorbing J^- and Br^- ions exert a noticeable accelerating effect already at rather low concentrations, whereas SO_4^{2-} and Cl^- ions, which have lower adsorption capacity, accelerate the anodic process only at comparatively high concentrations. However, in this case it is difficult to explain, for example, the linear dependence of i_a on the concentration of NaJ, as well as the independence of the rate of the cathodic process from the concentration of NaJ in the region of high concentrations*. Therefore it seems more probable to us that halide ions (except F^-) and sulfate take a direct part in the anodic process of indium ionization, although for a complete explanation of the observed effects, especially in the case of low concentrations of J^- and Br^-, it is apparently also necessary to take into account the influence of changes in the ψ_1-potential.

We express our deep gratitude to Ya. M. Kolotyrkin for valuable advice in discussing the results of this work.

Scientific-Research Physicochemical Institute
named after L. Ya. Karpov

Received
12 VI 1959

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* To explain this effect, one would have to assume that only In^{3+} ions participate in the electrode process, and that the accelerating influence of the ψ_1-potential on the cathodic process is exactly compensated by the slowing of the cathodic process as a result of a decrease in the concentration of In^{3+} ions with increasing NaJ concentration.

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

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