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## Abstract

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# THE INFLUENCE OF FLUORIDE IONS ON THE ANODIC DISSOLUTION OF INDIUM AMALGAM AND SOME REGULARITIES OF ELECTRODE PROCESSES INVOLVING COMPLEXES

*(Presented by Academician A. N. Frumkin, 11 VII 1962)*

Under conditions of complex formation, the processes of ionization and discharge of metal ions, generally speaking, may proceed by two different paths. First, simple hydrated metal ions may participate in the electrochemical stage of the process; thus, for example, in an anodic process the complex ions predominating in solution are formed as a result of a subsequent chemical reaction between the simple metal ions and addends, taking place in solution. Second, complexes may form and discharge directly at the electrode ([1]-[3]). Although the latter mechanism is at present generally accepted, under some conditions the electrode process may also proceed by the first path. One of the criteria for whether the process proceeds by the first or the second path may be the character of the dependence of the rate of the anodic process and of the exchange current on the concentration of addends (provided that the rate of the overall process is limited by the electrochemical stage). In the first case the rate of the anodic process at constant potential should not change with increasing addend concentration (the exchange current should then decrease); in the second case the rate of the anodic process should increase.

By combining radiochemical and electrochemical measurements we have shown ([4]) that at constant potential the rate of the anodic process on indium amalgam increases with increasing concentration of halide ions, and the conclusion was drawn that the corresponding indium complexes are formed directly, i.e., the electrode process proceeds by the second mechanism. It is of interest to study the influence on the anodic process on indium amalgam of fluoride ions, with which indium gives more stable complexes than with other halide ions ([5]). Since fluoride ions do not possess specific adsorption and do not exert an activating effect on the cathodic process of discharge of indium ions ([6]), it may be assumed that in this case the first mechanism will be observed.

The experimental procedure and conditions have been described earlier ([4]); the

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

influence of fluoride ions was studied by recording ordinary polarization curves in combination with radiochemical measurements for 0.1 $M$ indium amalgam in a solution of 0.01 $M$ $In(ClO_4)_3$ + $NaClO_4$ + $HClO_4$ with additions of NaF (0.01-0.2 $M$) at constant ionic strength (3$M$) and acidity (pH 1.3)*.

Judging from the character of the dependence of the equilibrium potential on fluoride concentration, at NaF concentrations of 0.01 $M$ and higher the solution is dominated by fluoride complexes of indium, which agrees well with the calculation of the concentration of $In^{3+}$ ions from the stability constants of $InF^{2+}$ and ${InF_2}^+$ ($^5$). From Fig. 1 it is seen that with increasing NaF concentration the exchange current decreases, the values of $i_0$ lying on a straight line with a slope of $0.025 \pm 0.005$ V, i.e., falling on the continuation of the curve of the true rate of the anodic process corresponding to the solution without additions of $F^-$ ions ($^4$). Thus, fluoride ions do not affect the position of the anodic curve. The dependence of $i_0$ on potential, practically coinciding with the iso-

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* Work with $F^-$ ions involves difficulties, since in order to avoid precipitation of $In(OH)_3$ it is necessary to maintain low pH; however, upon acidification an appreciable concentration of HF is formed (increasing with increasing NaF content), which reacts with glass to give fluorosilicates that may affect the kinetics of the electrode process.

shown in Fig. 1, is observed when measuring the exchange current in solutions with a variable concentration of $In(ClO_4)_3$ (7), when the values of $i_0$ for different concentrations of $In^{3+}$ ions also fall on a single curve of the true rate of the anodic process. Consequently, fluoride ions do not participate in the stage of indium ionization, which can be expressed by the equation $In \rightarrow In^{3+} + 3e$; their action is reduced to binding $In^{3+}$ ions

**Fig. 1.** Dependence of the exchange current (a/$cm^2$) on the potential (normal hydrogen scale) for different NaF concentrations: *a*—0; *b*—0.01 $M$; *v*—0.02 $M$; *g* —0.05 $M$; *d*—0.1 $M$; *e*—0.2 $M$

**Fig. 2.** Polarization curves for different NaF concentrations: 1—0; 2—0.01 $M$; 3—0.05 $M$; 4—0.1 $M$; 5—0.2 $M$

into complexes, as a result of which the concentration of $In^{3+}$ ions decreases and $i_0$ is lowered. The decrease in $i_0$ with increasing NaF concentration should lead to a decrease in the rate of the cathodic process. This effect is clearly illustrated by the shift of the cathodic curves with increasing NaF concentration (Fig. 2). If not simple but complex indium ions ($\mathrm{InF}^{2+}$) participated in the cathodic process, then at NaF concentrations above 0.01 *M* the content of these complexes would remain practically unchanged, and the rate of the cathodic process at constant potential should not change*. As can be seen from Fig. 2, at the highest NaF concentrations (0.1-0.2 *M*) the rate of the cathodic process up to a potential of −0.60 V ceases to decrease with increasing fluoride concentration, and at more negative potentials this rate even increases with increasing NaF content; it is possible that under these conditions higher fluoride complexes ($\mathrm{InF}_2^+$ or $\mathrm{InF}_3$) can also participate in the electrode process. In this case, the values of the exchange current of the process of direct discharge of the complexes, naturally, should no longer lie on the continuation of the anodic curve presented in Fig. 1, since for this process, as the NaF concentration increases, the anodic curve should shift to the right (4); this may lead to the appearance, on the curve of the dependence of the exchange current on the NaF concentration (or on the potential), of a minimum**, which will correspond to the transition from the electrode process involving simple hydrated indium ions to the process of direct discharge of complex particles.

In the general case, taking into account the possibility of direct participation in the electrode process not only of the complexes $\mathrm{MX}_p^{(n-p)+}$ predominating in solution, but also of other complexes in equilibrium with them, the process of anodic dissolution of a metal can be represented as

a combination of three parallel processes:

A.

$$\mathrm{M} \rightarrow \mathrm{M}^{n+} + ne; \qquad \mathrm{M}^{n+} + p\mathrm{X}^- \rightleftarrows \mathrm{MX}_p^{(n-p)+}.$$

B.

$$\mathrm{M} + q\mathrm{X}^- \rightleftarrows \mathrm{MX}_q^{(n-q)+} + ne; \qquad \mathrm{MX}_q^{(n-q)+} + (p-q)\mathrm{X}^- \rightleftarrows \mathrm{MX}_p^{(n-p)+}.$$

C.

$$\mathrm{M} + p\mathrm{X}^- \rightleftarrows \mathrm{MX}_p^{(n-p)+} + ne.$$

Schemes A and C correspond to the cases considered of electrode processes involving, respectively, simple hydrated metal ions and complexes predominating in solution; scheme B corresponds to a case frequently encountered in practice, when complexes $\mathrm{MX}_q^{(n-q)+}$ that do not predominate in solution participate in the electrode process (as a rule, the condition $q < p$ is observed, although sometimes $q > p$). The overall rate of the anodic and cathodic processes can be expressed by the equations:

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* The unusually high slope of the cathodic polarization curves (0.40-0.50 V) is apparently due to the presence of the preceding chemical reaction.

** In our experiments this minimum could not be detected, since, for the reasons indicated above, we could not work with NaF concentrations above 0.2 *M*.

$$i_a = k'_{\mathrm{A}}[\mathrm{M}]e^{\beta_1 \varphi F/RT} + k'_{\mathrm{B}}[\mathrm{M}][\mathrm{X}^-]^q e^{\beta_2 \varphi F/RT} + k'_{\mathrm{C}}[\mathrm{M}][\mathrm{X}^-]^p e^{\beta_3 \varphi F/RT}; \qquad (1)$$

$$i_k = k''_{\mathrm{A}}[\mathrm{M}^{n+}]e^{-\alpha_1 \varphi F/RT} + k''_{\mathrm{B}}[\mathrm{MX}_q^{(n-q)+}]e^{-\alpha_2 \varphi F/RT} + k''_{\mathrm{C}}[\mathrm{MX}_p^{(n-p)+}]e^{-\alpha_3 \varphi F/RT}. \qquad (2)$$

Using expressions for the dependence of the equilibrium potential on the concentration of the reacting species, as well as the conditions of equilibrium between different complexes in solution, from equations (1) and (2) it is not difficult to obtain the following expression for the dependence of the total exchange current on the concentration of the addend (the condition $\alpha + \beta = n$ [9] is adopted, as are the assumptions $\alpha = \alpha_1 = \alpha_2 = \alpha_3$ and $\beta = \beta_1 = \beta_2 = \beta_3$):

$$i_0 = [\mathrm{M}]^{\alpha/n}[\mathrm{MX}_p^{(n-p)+}]^{\beta/n}\left[{}_{\mathrm{A}}i_0^0[\mathrm{X}^-]^{-\beta p/n} + {}_{\mathrm{B}}i_0^0[\mathrm{X}^-]^{q-(\beta p/n)} + {}_{\mathrm{C}}i_0^0[\mathrm{X}^-]^{\alpha p/n}\right], \qquad (3)$$

where ${}_{\mathrm{A}}i_0^0$, ${}_{\mathrm{B}}i_0^0$, and ${}_{\mathrm{C}}i_0^0$ denote the standard exchange-current densities corresponding to concentrations of the reacting species equal to unity. As is evident from equations (1-3), in the case where mechanism A predominates, when the second and third terms in these equations can be neglected, at constant potential the rate of the anodic process $i_a$ does not depend on the concentration of the addend, whereas the rate of the cathodic process $i_k$ and the exchange current $i_0$ decrease with increasing concentration of $\mathrm{X}^-$, as is observed for fluoride complexes of indium (see Fig. 1 and Table 1), and also for oxalate complexes of zinc [2, 3] and cyanide complexes of cadmium [10]. Conversely, in the case where mechanism C predominates, $i_a$ and $i_0$ increase, while $i_k$ does not change with increasing concentration of the addend. Finally, in the case where mechanism B predominates, at $\varphi = \mathrm{const}$, $i_a$ also increases with the concentration of $\mathrm{X}^-$, whereas $i_k$ may either decrease (when $q < p$) or increase (when $q > p$), and the dependence of $i_0$ on the concentration of $\mathrm{X}^-$ will correspondingly be more complex*.

It follows from equation (3) that with increasing addend concentration the exchange current should at first decrease; however, with a further increase, the relative contribution of mechanisms B and C should grow, and therefore in the general case one may expect the appearance of a minimum on the curve of the dependence of the exchange current on the concentration of the addend (or on the potential)**. However, as is evident from Table 1, only for the ion $\mathrm{F}^-$ is a decrease in $i_0$ observed with increasing concentration of the addend; in the case of the ions $\mathrm{SO}_4^{2-}$ and $\mathrm{Cl}^-$, $i_0$ is practically independent of the concentration of the additive, whereas even small additions of NaBr and NaJ cause a noticeable increase in $i_0$. The cause of this phenomenon becomes clear if one takes into account that the exchange current increases in the series $\mathrm{F}^- < \mathrm{SO}_4^{2-},\ \mathrm{Cl}^- < \mathrm{Br}^- < \mathrm{J}^-$ (see Table 1),

* This case apparently corresponds to chloride and sulfate complexes of indium (see Table 1). In the particular case of mechanism B, when $p = 0$ (i.e., simple species predominate in solution, but complexes are discharged), $i_a$, $i_k$, and $i_0$ should increase with increasing concentration of $X^-$, as is observed for indium at low concentrations of NaJ [4].

** Since the standard exchange current of the predominating complex ${}_{\mathrm{B}}i_0^0$, generally speaking, should decrease with increasing stability of this complex, then, as analysis of equations (1-3) shows, this minimum should be the deeper the more stable the metal complexes with the given addend. The appearance of a minimum on the curve of the dependence of the exchange current on the concentra-

**Table 1**

Exchange currents (A/cm$^2$) for 0.1 M In(Hg) + 0.01 M $In(ClO_4)_3$ with additions of various salts ($^4$) at a constant ionic strength of 3 M (in the absence of additions $i_0 = 1.7 \cdot 10^{-4}$ A/cm$^2$)

| Salt | 0.02 M | 0.1 M | 0.5 M | 2.0 M |
|---|---|---|---|---|
| NaF | $9.1 \cdot 10^{-5}$ | $1.6 \cdot 10^{-5}$ | – | – |
| NaCl | – | $1.7 \cdot 10^{-4}$ | $1.7 \cdot 10^{-4}$ | $8.3 \cdot 10^{-4}$ |
| NaBr | $3.8 \cdot 10^{-4}$ | $1.1 \cdot 10^{-3}$ | $2.9 \cdot 10^{-3}$ | $5.0 \cdot 10^{-3}$ |
| NaI | $1.9 \cdot 10^{-3}$ | $4.7 \cdot 10^{-3}$ | $8.7 \cdot 10^{-3}$ | – |
| $Na_2SO_4$ | – | $3.0 \cdot 10^{-4}$ | $1.7 \cdot 10^{-4}$* | – |

* For 0.6 M $Na_2SO_4$.

which coincides with the sequence of increasing adsorption ability of these anions on the surface of mercury. As a result of simultaneous interaction both with the electrode surface and with the metal ion in the complex, easily polarizable halide anions (except for the $F^-$ ion) accelerate the stage of discharge and formation of these complexes ($^{13}$-$^{15}$)*, i.e., the standard exchange currents of the complexes ($b_i^0$ and $b_i^0$ in equation (3)) considerably exceed the standard exchange current of the simple ions $Ai_0^0$, and therefore, in the presence of even small additions of addend, the electrode process proceeds practically only by mechanism B or C. Consequently, when assessing the influence of complex formation on the kinetics of the electrode process, it is necessary to take into account not only the stability of the complex compound of the metal with the given addend, but also the ability of the addend to be adsorbed on the electrode surface and to facilitate the discharge—ionization stage of the complex**. The activating action of such anions included in the composition of the complex often masks the effect of complex formation, which, generally speaking, should lead to a decrease in the exchange current, as is observed in the case of addends that do not possess specific adsorption, such as, for example, the $F^-$ ion.

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The addition of NaCN was observed for cadmium amalgam ($^{2}$) and for the silver electrode ($^{11}$); comparison of the values of the exchange current on the silver electrode in $AgNO_3$ solution ($^{1}$,$^{2}$) and in solutions containing ammine complexes of silver ($^{11}$) indicates that in this case as well the analogous curve must pass through a deep minimum.

* Such anions apparently form an electron-conducting bridge between the central ion of the complex and the electrode ($^{4}$,$^{16}$); for a complete interpretation of their catalytic influence it is also necessary to take into account the change in the structure of the double layer as a result of their adsorption, which may, in particular, cause some increase in the rate of process A.

** Analogous regularities are observed in the discharge of bismuth complexes ($^{17}$).

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

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