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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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V. V. GORODETSKII, V. V. LOSEV

STUDY OF ELECTRODE PROCESSES ON BISMUTH AMALGAM BY A RADIOCHEMICAL METHOD

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To elucidate the kinetic regularities and mechanism of the processes of anodic dissolution and electrodeposition of metals, it is first of all necessary to know the principal kinetic parameters of these processes, namely the exchange current, transfer coefficients, and electrochemical reaction orders. To solve this problem in the case of amalgam electrodes, alongside various nonstationary methods, a method based on the combination of radiochemical and electrochemical measurements was used ($^{1-4}$). Since in the literature there are almost no data on the kinetic parameters of electrode processes for metals with valences higher than two, it is of interest to investigate bismuth amalgam by this method. A special feature of bismuth amalgam is that its equilibrium potential lies in the region of positive surface charge, and this may have a substantial effect on the kinetics of the electrode process. In the discharge of simple bismuth ions on a dropping mercury electrode in the absence of activating anions, irreversible waves are observed ($^{5-7}$), and the exchange current between bismuth amalgam and Bi^{3+} ions is comparatively low (^{8,9}).

Fig. 1. True anodic curve (1) and polarization curves (2) for
$c_a = 0.11\,M$ and $c_p = 2.8 \cdot 10^{-3}\,M$

We have investigated the regularities of the processes of discharge and ionization of bismuth at an amalgam electrode ($5 \cdot 10^{-5}$—$0.3\,M$) in solutions of $Bi(ClO_4)_3$ ($2 \cdot 10^{-6}$—$0.02\,M$) using the radioactive isotope Bi^{210}. All experiments were carried out at 20° in $HClO_4$ solutions of constant ionic strength ($2M$).

Figure 1 presents the dependence, found by the radiochemical method, of the true rate of the anodic process i_a on the potential (curve 1), together with or-

Fig. 2. True anodic curves and polarization curves for various amalgam concentrations

Figure 2: Fig. 2. True anodic curves and polarization curves for various amalgam concentrations

dinary polarization curves recorded by current (curves 2). As can be seen, the anodic process proceeds at an appreciable rate even under strong cathodic polarization; moreover, in the region of the equilibrium potential a linear dependence is observed between the potential and the logarithm of i_a.* This linear segment, with slope coefficient $b'_a = 0.033 \pm 0.001$ V, can be obtained only from radiochemical measurements, since it does not appear on the anodic polarization curve. The transfer coefficient calculated from it is equal to $\beta = 2.3RT/b'_{aF} = 1.76 \pm 0.05$. If, at a given amalgam concentration, the exchange currents i_0 are measured at different concentrations of bismuth ions in solution, the obtained values of i_0 fall on the same linear segment of the true anodic curve. This result shows— shows that the true anodic curve, recorded by the radiochemical method at a given concentration of $Bi(ClO_4)_3$, coincides with the anodic curve constructed from exchange currents at the same amalgam concentration, as should be expected under conditions in which the rate of the electrode process is limited by the discharge-ionization stage (^{10}). This agreement also shows that the rate of the anodic process does not depend on the concentration of bismuth ions.

With a certain shift from the equilibrium potential in the positive direction, a bend is observed on the curve ($\varphi - \lg i_a$) (Fig. 1), and at more positive potentials a second linear segment appears, with a higher slope $b'_a = 0.074 \pm 0.003$ V, $\beta = 0.78 \pm 0.03$. This bend is not associated with concentration polarization in the amalgam (it appears in the region of current densities two orders of magnitude lower than the anodic limiting current, equal to 0.38 A/cm^2) or with precipitation of $Bi(ClO_4)_3$ on the surface of the amalgam as a result of an increase in the near-electrode concentration of Bi^{3+} ions, since the solubility of $Bi(ClO_4)_3$ is sufficiently high (~ 0.5 M). When the second Tafel segment of the anodic curve is extrapolated to the equilibrium potential, the extrapolated exchange current obtained exceeds the true one by almost a factor of 5.*

Fig. 2. True anodic curves and polarization curves for various amalgam concentrations
(1—0.11 M; 2—0.01 M; 3—$5 \cdot 10^{-4}$ M), $c_p = 2.8 \cdot 10^{-3}$ M for 1 and $c_p = 5 \cdot 10^{-3}$ M for 2 and 3

The dependence of i_a on the potential for various amalgam concentrations c_a, together with the corresponding anodic polarization curves, is presented in Fig.

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* Upon displacement from the equilibrium potential in the positive direction, the true-rate curve of the anodic process, obtained by the radiochemical method, coincides with the ordinary polarization curve. This coincidence shows that the current efficiency of the anodic process of bismuth ionization is 100% (^{10}).

Fig. 3

Figure 3: Fig. 3

2. The above-mentioned agreement of the true anodic curves obtained by the radiochemical method with those constructed from exchange currents at various solution concentrations makes it possible to record these curves by either method, depending on which of them is experimentally more convenient. In Fig. 2, curve 1 was recorded at a constant concentration of Bi^{3+} ions (c_p), while curves 2 and 3 were obtained, up to potential values equal respectively to 0.240 and 0.267 V, from exchange currents at different c_p, and at more positive potentials from radiochemical data under anodic polarization. In the region of high anodic current densities, the polarization curves were corrected for concentration polarization in the amalgam using experimental values of the limiting current (for example, at $c_a = 5 \cdot 10^{-4}$ M (curve 3), $i_a^d = 1.45 \cdot 10^{-3}$ A/cm^2). As c_a increases, the anodic curves shift in the negative direction; in this case the slope coefficients of both linear segments remain unchanged, while the potential of the bend point on the anodic curve (more precisely, the potential of the intersection point of the two linear segments) shifts in the negative direction. In Fig. 2 the dashed straight lines are drawn at $\varphi = 0.20$ V and at $\varphi = 0.35$ V; the points of intersection of the anodic curves with these straight lines represent the values of i_a at constant potential, corresponding respectively to the first and second linear portions. The dependences of i_a on c_a found in this way from Fig. 2, and also from other experiments, are presented in Fig. 3. The slopes of the straight lines corresponding to $\varphi = 0.20$ V and $\varphi = 0.35$ V are, respectively, 1.03 and 0.76. Consequently, both in the region of low slope and in the region of high slope, the rate of the anodic process is directly proportional to the concentration of the amalgam.* As already noted, in the region of low slope i_a does not depend on the concentration of Bi^{3+} ions; in the region of high slope the same conclusion follows from the coincidence of anodic polarization curves recorded in solutions with c_p from $1 \cdot 10^{-4}$ to $2 \cdot 10^{-2}$ M (^{11}). The results obtained by us can be expressed by the equation $i_a = k[\mathrm{Bi}] \exp(\beta \varphi F / RT)$, where the transfer coefficient β is 1.76 and 0.78, respectively, for the regions of low and high slopes of the curve $(\varphi\text{—}\lg i_k)$.

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* It should be noted that although in the present case the anodic limiting current exceeds i_0 by more than three orders of magnitude, i.e., favorable conditions exist for conducting polarization measurements in the kinetic region, the detection of two Tafel segments on one curve and the determination of the two corresponding values of i_0 proved possible only owing to the combination of electrochemical measurements with radiochemical ones. This result illustrates the higher resolving power of the radiochemical method in comparison with the method of stationary polarization curves.

Fig. 4

Figure 4: Fig. 4

Fig. 3. Dependence of i_a on c_a at $\varphi = \text{const}$: upper curve—at $\varphi = 0.2$ V; lower curve at $\varphi = 0.35$ V

To clarify the dependence of the true rate of the cathodic process i_k on the potential, exchange currents were measured at a constant concentration of $\mathrm{Bi(ClO_4)_3}$ ($5 \cdot 10^{-3}$ M) and various c_a (from $5 \cdot 10^{-5}$ to 0.3 M). As can be seen from Fig. 4, the true cathodic curve thus obtained (^{3,10}) is linear and has a slope coefficient of 0.049 ± 0.003 V, corresponding to a transfer coefficient

$$\alpha = (2.3RT/F)\left(d\varphi_p/d\lg i_0\right)_{c_p} = 1.18 \pm 0.07.$$

This value of α somewhat exceeds the value $\alpha = 0.99$ found from polarographic data (^{7}) for 1 M HClO (recalculated to the normalization adopted by us, $\alpha+\beta = 3$ (^{3})). To estimate the dependence of i_k on the concentration of Bi^{3+} ions (c_p), the true anodic curves recorded from exchange currents were used (curves 2 and 3 in Fig. 2): through the points corresponding to exchange currents at different c_p, cathodic straight lines with a slope of 0.049 V were drawn, and their points of intersection with the constant-potential line (^{10}) were determined. Judging from the slope of the curves constructed from these data ($\lg i_k$—$\lg c_p$), equal to 0.91, the true rate of the cathodic process is proportional to the concentration of Bi^{3+} ions. The presence of a linear dependence between the logarithm of the rate of the anodic and cathodic processes and the potential, the results of determining the electrochemical reaction orders, and also the closeness of the sum of the transfer coefficients to 3 ($\alpha + \beta = 2.96$) in the region of potentials of low anodic slope show that in this region the rate of the electrode process is determined by the discharge-ionization stage. Generally speaking, the condition $\alpha + \beta = 3$ must be satisfied

Fig. 4. True cathodic curve, constructed from exchange currents at $c_p = 5 \cdot 10^{-3}$ M for different c_a (from $5 \cdot 10^{-5}$ to 0.3 M): *a*—0.3; *b*—0.1; *v*—$4 \cdot 10^{-2}$; *g*—$1 \cdot 10^{-2}$; *d*—$5 \cdot 10^{-3}$; *e*—$4 \cdot 10^{-3}$; *zh*—$2 \cdot 10^{-3}$; *z*—$5 \cdot 10^{-4}$; *i*—$2 \cdot 10^{-4}$; *k*—$5 \cdot 10^{-5}$

for the anodic and cathodic processes and the potential; the results of determining the electrochemical reaction orders, as well as the closeness of the sum of the transfer coefficients to 3 ($\alpha + \beta = 2.96$) in the region of potentials of low anodic slope, show that in this region the rate of the electrode process is determined by the discharge-ionization stage. Generally speaking, the condition $\alpha + \beta = 3$ must be observed—

* Generally speaking, it follows from this result that the inflection points on anodic curves corresponding to different c_a should lie at constant potential; the shift of the potential of the inflection point in the negative direction with

increasing c_a, observed experimentally (Fig. 2), is due to the fact that for the linear portion with high slope the reaction order with respect to the amalgam is somewhat lower than first (0.76); the reason for this deviation is not clear.

be observed also in the region of potentials of high anodic slope, and, consequently, the inflection on the true anodic curve must correspond to an inflection on the true cathodic curve in the same region of potentials (0.28 V); as is seen from Fig. 4, we were able to record the latter curve only at more negative potentials, and therefore it was not possible to detect an inflection on it.

Calculation of the standard exchange current ([12,3]) from the equation $i_0 = i_0^0 c_a^{\alpha/3} c_p^{\beta/3}$, using our data and experimental values of α and β, gives the value $i_0^0 = 1 \cdot 10^{-2}$ A/cm^2.*

To elucidate the mechanism of the discharge-ionization process on bismuth amalgam, the presence of two linear sections on the true anodic curve, as well as the discrepancy between the exchange currents extrapolated from the region of high anodic slope and the true exchange currents, is of essential importance. This effect, which apparently cannot be interpreted by assuming that the electrode process proceeds in a single elementary act ($\mathrm{Bi} \rightleftarrows \mathrm{Bi}^{3+} + 3e$), receives a satisfactory explanation on the basis of the concept of the stepwise course of multielectron processes with the participation of metallic electrodes ([2,3,14,15]). Indeed, as the analysis of the equations for an ordinary polarization curve recorded by current and for the true anodic curve for a three-stage process, obtained by Vetter' s method ([16]), shows, under conditions of comparable rates of the individual stages, an inflection may appear on the curve $(\varphi - \lg i_a)$ at potentials more positive than the equilibrium potential, and a linear section with low slope may appear in the region of the equilibrium potential; moreover, the exchange current extrapolated from the far anodic region must exceed the true exchange current measured at the equilibrium potential. Our data on transfer coefficients indicate that, in the region of low slope, where the relations $1 < \alpha < 2$ and $1 < \beta < 2$ are fulfilled, the limiting stage is $\mathrm{Bi}^{+} \rightarrow \mathrm{Bi}^{2+} + e$, whereas in the region of potentials of high slope $(0 < \beta < 1)$ the rate of the process is determined by the stage $\mathrm{Bi} \rightarrow \mathrm{Bi}^{+} + e$. The easier removal of the third electron in the case of bismuth, in comparison with other metals ([14]), is apparently due to the fact that in this stage it is not simple hydrated bismuth ions (as in the other stages) that participate, but hydrolyzed particles ($\mathrm{BiOH}^{+} \rightarrow \mathrm{BiOH}^{2+} + e$), whose adsorption and discharge on the positively charged surface of the amalgam proceed considerably more readily ([17]).

Physical Chemistry Institute
named after L. Ya. Karpov

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* The rate constant calculated from this value ($k = 3.5{\cdot}10^{-5}$ cm/sec^{-1}) is almost an order of magnitude lower than that found by Randles (^{8}) by the alternating-current method. Judging from our data on the strong accelerating action of small concentrations of halide ions on this process (^{11}), this discrepancy may be associated with the presence, in Randles' s experiments, of a small admixture of chlorine ions. Indeed, in Randles' s experiments, addition of $1 \cdot 10^{-3}$ M Cl^{-} caused an increase of k by only a factor of 5–6, whereas in our experiments,

with careful removal of Cl^- ions from the initial solutions, the same addition led to a 30-fold increase in the exchange current. At high concentrations of Cl^- ($1M$), the exchange current increases so much that only its lower limit can be estimated ([8]); under these conditions the rate of isotopic exchange is limited by diffusion of the radioactive particles, and the radiochemical method gives an understated value of the exchange current ([13,3]).

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

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