ELECTROCHEMICAL OSCILLATIONS ON POLAROGRAPHIC I–t CURVES IN BROMATE SOLUTIONS

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Polarographic I–t curves obtained with a dropping mercury electrode in solutions of sulphuric acid and bromate ions show oscillations in the region of positive potentials. These are related with the formation of Hg(II) bromate as anodic oxidation product, which is in turn reduced to Hg(I) bromate forming a passivating layer on the Hg electrode. The layer is mechanically disrupted during growth of the drop, whereby the electrode is reactivated. and the process goes on giving rise to current oscillations.

Oscillations of the potential in electrochemical systems have been observed since 1828, the first observation being concerned with periodic deposition of silver on iron in solutions of silver nitrate[1]. However, the discovery of the Belousov–Zhabotinskii reaction in the fifties[2,3] has stimulated the interest in oscillations in both homogeneous and heterogeneous systems and started their systematic study. Wojtowicz[4] wrote a review about electrochemical oscillations in 1973, when a new interdisciplinary field of research appeared, namely synergetics[5,6], dealing with dissipative structures.

Since the Belousov–Zhabotinskii reaction is related with the chemistry of bromates, we have concentrated during recent years on electrochemical oscillations based on the reactions of bromates. The simplest system, a dropping mercury electrode in a solution of bromate ions and H_2SO_4, shows oscillations of the polarographic current and of the surface tension of mercury[7]. It also shows current oscillations in the presence of phenol, due to alternating transitions between the active state of the electrode and its passive state caused by a surface film[8].

In the cited works[7,8], we observed oscillations of the polarographic current under potentiostatic conditions; the present work is devoted to the study of oscillation phenomena occurring during the drop time of the dropping mercury electrode, i.e. on the I–t curves.

Electrochemical oscillations on the I–t curves were described already by Jenšovský[9] in a polarographic study of periodates in strongly alkaline media. Peizker[10] elucidated certain discontinuities on the polarographic curves in terms of the Kaufman instability conditions occurring in the polarographic circuit. Heyrovský[11] described oscillations on the I–t curves near the maximum on the polarographic wave of aluminium.

EXPERIMENTAL

Polarographic $I-t$ curves were recorded on an OH 105 polarograph (Radelkis, Hungary) with a dropping mercury electrode at a rate of flow of mercury $1.55\ \text{mg s}^{-1}$ and a drop time 4.5 s in redistilled water at a height of mercury column 75 cm. Some experiments were made with a stationary Hg drop with a surface area of $0.20\ \text{cm}^2$. The reaction solution was placed in a Kalousek cell with a separated $2\text{M-Hg}_2\text{SO}_4/\text{Hg}$ reference electrode and a thermostated mantle piece, connected with an ultrathermostat U 15 VEB (Medingen G.D.R.). The instantaneous current–time curves were recorded under potentiostatic conditions, the damping of the recorder being set to zero.

Mercury(II) bromate was prepared by crystallization from a solution[12] prepared by dissolving NaBrO_3 and $\text{Hg(NO}_3)_2$ in the stoichiometric ratio in a hot solution of 3M-HNO_3. The product, $\text{Hg(BrO}_3)_2.2\ \text{H}_2\text{O}$, was recrystallized from aqueous 0.1M-HNO_3. Mercury(I) bromate was prepared by recrystallization from a solution prepared by dissolving NaBrO_3 and HgNO_3 in the stoichiometric ratio in 1.5M-HNO_3. All chemicals were of reagent grade. Mercury was of polarographic grade, 99.999% (Služba výzkumu, Bechyně) and gelatin was according to the Czechoslovak Pharmacopoeia (ČSL 3, Medika).

RESULTS

It can be seen from the polarographic $I-E$ curve for NaBrO_3 in a solution of sulphuric acid (Fig. 1) that a maximum related with adsorption phenomena[13] appears in the region of positive potentials. The $I-t$ curves show a non-monotonous or periodic course at potentials from $+0.02$ to 0.05 V against the Hg_2SO_4 electrode. For ex-
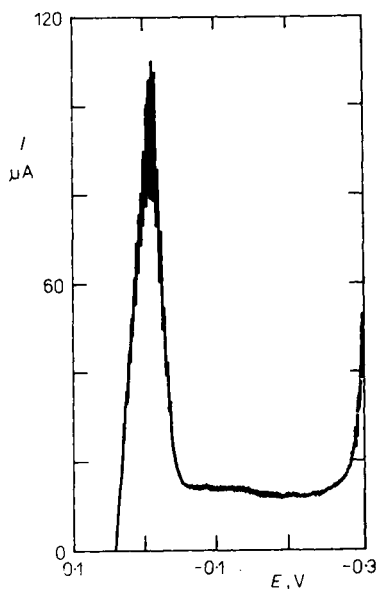

FIG. 1

Maximum on the polarographic $I-E$ curve in a solution of 0.1M-NaBrO_3 and 1.5M- -H_2SO_4 at $20°\text{C}$

ample, in a solution of $1.5M$-H_2SO_4 and $0.1M$-$NaBrO_3$ at $+0.04$ V and 20°C the instantaneous anodic current increases from the beginning of the drop time to a maximum value, then decreases, and during further three seconds passes through one or two more maxima (Fig. 2). Although the I–t curves are not fully reproducible, their periodic course always takes place. Better reproducibility is attained at an elevated temperature of 40°C (Fig. 3). When the potential is shifted to negative values, we obtain cathodic current (Fig. 1) since the mentioned maximum increases. Also the instantaneous cathodic current passes through several maxima and minima (Fig. 4) during the drop life.
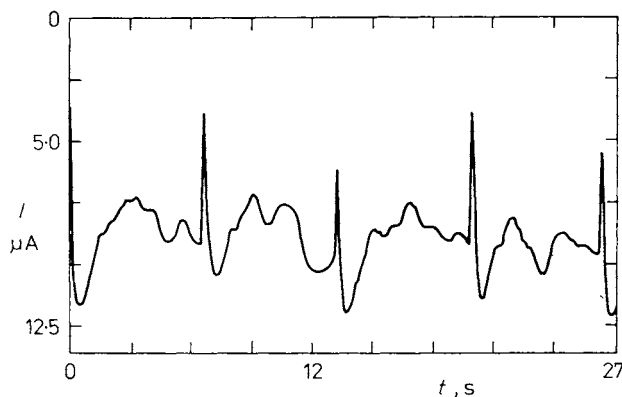

FIG. 2

Polarographic I–t curves in a solution of $0.1M$-$NaBrO_3$ and $1.5M$-H_2SO_4 at $+0.04$ V, 20°C
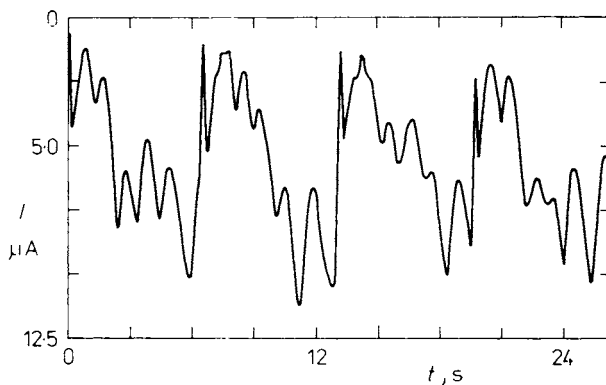

FIG. 3

Polarographic I–t curves for bromate ions at 40°C. Conditions as in Fig. 2
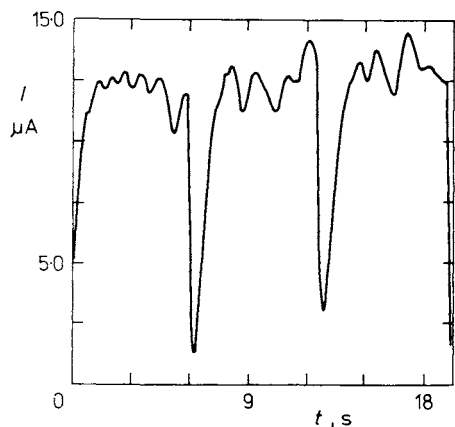
FIG. 4

Polarographic $I–t$ curves for bromate ions in the cathodic region. Same solution as in Fig. 2, $+0.03$ V, $30°C$
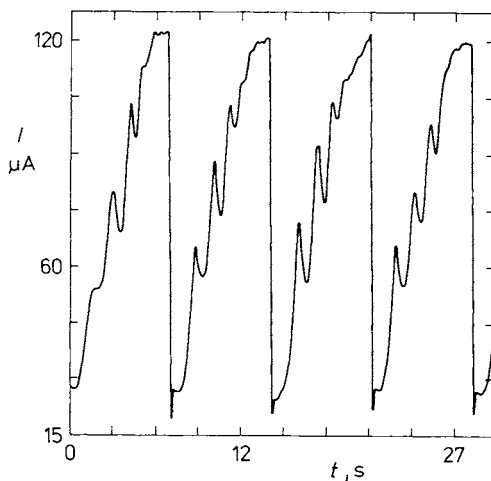

FIG. 5

Polarographic $I–t$ curves for mercury(II) bromate. $1.5M$-H_2SO_4 and $0.01M$-$Hg(BrO_3)_2$, 0.0 V, $40°C$
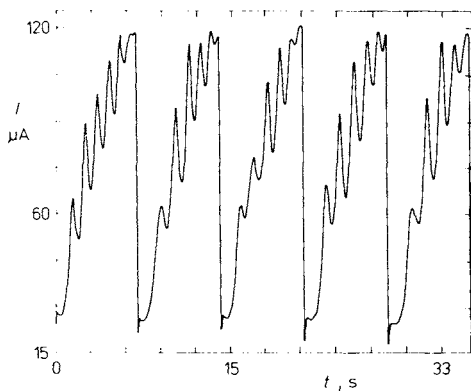

FIG. 6

Influence of electrode potential on the number of oscillations on the $I–t$ curves. Conditions as in Fig. 5, -0.005 V
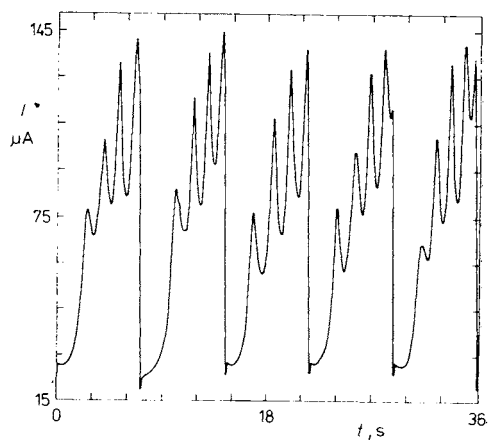

FIG. 7

Influence of electrode potential on the amplitude of oscillations on the $I–t$ curves. Conditions as in Fig. 5, -0.01 V

Addition of 27 mg of $Hg_2(BrO_3)_2$ into 25 ml of a solution of $0 \cdot 1M$-$NaBrO_3$ and $1 \cdot 5M$-H_2SO_4 at 40°C causes a decrease of the oscillation amplitude (by about 70%) and period (by about 60%).

If the dropping mercury electrode is replaced by a stationary mercury drop, no oscillations take place. The time course of the current here corresponds to a change from the active to the passive state of the electrode: the anodic current increases to a maximum and then decreases.

As follows from the electrochemical study of bromates[13], at sufficiently positive potentials the anodic current in a solution of H_2SO_4 and bromate ions corresponds to the formation of $HgSO_4$ and $Hg(BrO_3)_2$. We therefore studied the I–t curves in solutions of sulphuric acid and $Hg(BrO_3)_2$.

The current–potential curve in a solution of $0 \cdot 01M$-$Hg(BrO_3)_2$ and $1 \cdot 5M$-H_2SO_4 is analogous to that in Fig. 1, however the maximum is higher by a factor of about 30. The course of the I–t curves (their oscillation character) depends not only on the temperature and potential of the electrode but also on the age of the solution and the duration of its contact with mercury. At the beginning of the experiment, the curves are nearly monotonous; after 120 min they show reproducible oscillations (Fig. 5). When the potential of the mercury dropping electrode is shifted from zero to $-0 \cdot 005$ V, the number of oscillations on the I–t curves increases (Fig. 6); when it is shifted to $-0 \cdot 01$ V, the number of oscillations decreases, but their amplitude increases (Fig. 7). When the potential shifts further to more negative values, the number of oscillations decreases further and at $-0 \cdot 02$ V they become sporadic and random. Also in this case, if the dropping mercury electrode is replaced by a stationary one, no oscillations are observed.

DISCUSSION

We explained the electrochemical oscillations in the systems Hg, HSO_4^-, BrO_3^- and Hg, HSO_4^-, BrO_3^-, phenol by simultaneous electroreduction of bromate ions, electro-oxidation of mercury and changes of its surface tension caused by the surface films of Hg_2SO_4 and Hg_2Br_2, and by adsorption of phenol on the surface of the dropping mercury electrode[7,8]. The present results concerning oscillations on the I–t curves lead us to the idea about the important role of Hg(II) and Hg(I) bromates.

Anodic oxidation of mercury in the presence of bromate ions very probable leads to $Hg(BrO_3)_2$, which in turn is converted to $Hg_2(BrO_3)_2$:

$$Hg \ + \ Hg(BrO_3)_2 \ \rightleftarrows \ Hg_2(BrO_3)_2 \, . \hspace{2cm} (A)$$
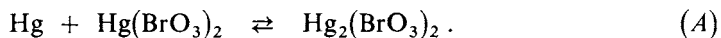
The oscillations on the I–t curves can be attributed to two counteracting processes, namely passivation of the electrode by the $Hg_2(BrO_3)_2$ film and activation caused by rupturing of the film as a result of the growth of the drop. The latter effect is in

accord with the observation that no oscillations take place on a stationary drop. Since oscillations are observed on the $I–t$ curves also in the cathodic region, electro-reduction of $Hg(BrO_3)_2$ can be considered as the back electrode process. This leads to the sparingly soluble $Hg_2(BrO_3)_2$, which is adsorbed and blocks the electrode surface, as evidenced by the fact that addition of $Hg_2(BrO_3)_2$ causes diminishing of the oscillation amplitude by up to 70%.

It can be concluded that the oscillations on the polarographic $I–t$ curves in solutions of bromate ions suitably supplement the phenomenology of electrochemical oscillations of bromates as described in our preceding communications[7,8].

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