

Electrochemical oscillations of the system $\text{Hg}|\text{HSO}_4^-|\text{BrO}_3^-$

A. OLEXOVÁ and L. TREINDL

*Department of Physical Chemistry, Faculty of Natural Sciences,
Komenský University, CS-842 15 Bratislava*

Received 17 January 1983

The electrochemical oscillations of the system $\text{Hg}|\text{HSO}_4^-|\text{BrO}_3^-$ which arise at a dropping mercury electrode in the solution of H_2SO_4 in the presence of sodium bromate in the interval of potentials $\langle +0.06 \text{ V}, +0.02 \text{ V} \rangle$ referred to the potential of the electrode Hg_2SO_4 ($c = 2 \text{ mol dm}^{-3}$)|Hg are described in this paper. The nonlinear increase in anodic current and linear increase in surface tension of the dropping mercury electrode periodically vary with time in the course of a few hours.

A probable mechanism giving rise to electrochemical oscillations which have not been described yet is discussed. The basis of this mechanism is simultaneous electroreduction of bromates and electrooxidation of mercury bringing about the formation of surface film.

В работе описываются электрохимические осцилляции системы $\text{Hg}|\text{HSO}_4^-|\text{BrO}_3^-$, возникающие на ртутном капельном электроде в растворе H_2SO_4 в присутствии бромата натрия в интервале потенциалов $\langle +0,06 \text{ в}, +0,02 \text{ в} \rangle$ по отношению к потенциалу электрода Hg_2SO_4 ($c = 2 \text{ моль дм}^{-3}$)|Hg. Нелинейное нарастание анодного тока и линейный рост поверхностного напряжения ртутного капельного электрода периодически изменяются на протяжении нескольких часов.

Обсуждается вероятный механизм возникновения до сих пор неописанных электрохимических осцилляций, основой которого является одновременно протекающее электровосстановление броматов и электроокисление ртути с образованием поверхностной пленки.

Oscillations of concentration of catalyst or intermediates as well as oscillations of any physicochemical quantity (potential, current, surface tension, etc.) belong to nonlinear phenomena which occur in systems sufficiently distant from thermodynamic equilibrium [1]. The oscillating behaviour of electrochemical systems was reviewed by Wojtowicz [2]. The electrochemical oscillations sometimes appear in the course of anodic dissolution of metals, anodic dissolution of nonmetallic compounds, cathodic processes or in electroosmosis.

The oscillations which come into existence in the course of polarographic reduction of the $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$, $PtCl_4^{2-}$, and CrO_4^{2-} anions were investigated by *Frumkin et al.* [3, 4]. *De Levie* [5] described the electrochemical oscillations accompanying reduction of the In^{3+} ions at mercury electrode in the solution of NaSCN. The oscillations of beating mercury heart were thoroughly investigated by *Keizer et al.* [6]. Their mechanism is based on the influence of voltage and adsorption on the value of mercury surface tension. The current oscillations at dropping mercury electrode due to retardation of the electrode processes involving the Cu^{2+} , Cd^{2+} , and Tl^+ ions by different surface-active substances were recently described by the authors of paper [7].

The aim of this study is to describe a new kind of electrochemical oscillations which were observed at dropping mercury electrode in sulfuric acid solution in the presence of bromates.

Experimental

The electrochemical oscillations were investigated polarographically by using dropping mercury electrode in a Kalousek vessel with separated Hg_2SO_4 ($c = 2 \text{ mol dm}^{-3}$)|Hg electrode which was equipped with a glass jacket joined to an ultrathermostat U 15 (VEB Kombinat Medizin und Labortechnik, GDR). The dropping mercury electrode had the flow rate $m = 1.22 \text{ mg s}^{-1}$ and drop time $t = 3.9 \text{ s}$ in distilled water for the height of mercury column $h = 64 \text{ cm}$. The polarographic measurements were carried out with a polarograph OH 105 (Radelkis, Budapest).

The chemicals used were anal. grade reagents: $NaBrO_3$ (Fluka), H_2SO_4 (VEB Laborchemie, Apolda), metallic mercury 99.999 % (Research Service), gelatine — Gelatina animalis CsL 3 (Medika). The solutions were prepared with redistilled water.

Results and discussion

If the dropping mercury electrode is polarized in the solution of $2 \text{ mol dm}^{-3} H_2SO_4$ containing bromates in the concentration range $3 \times 10^{-2} - 10^{-1} \text{ mol dm}^{-3}$, in the potential interval $\langle +0.06 \text{ V}, +0.02 \text{ V} \rangle$ with respect to the potential of Hg_2SO_4 ($c = 2 \text{ mol dm}^{-3}$)|Hg electrode, the mean anodic current (corresponding mainly to the formation of Hg_2SO_4) nonlinearly increases after a 10–15 min induction period and usually reaches its limiting value. Afterwards, it decreases to the initial value. The phenomenon periodically repeats itself with average oscillation period of 3–40 min according to the value of potential and bromate concentration (Fig. 1). The oscillation period is not constant during individual measurements and its length can deviate from the mean value even by 80 %. The dependence of oscillation period on potential and bromate concentration can be evaluated only qualitatively because the oscillation period has smaller

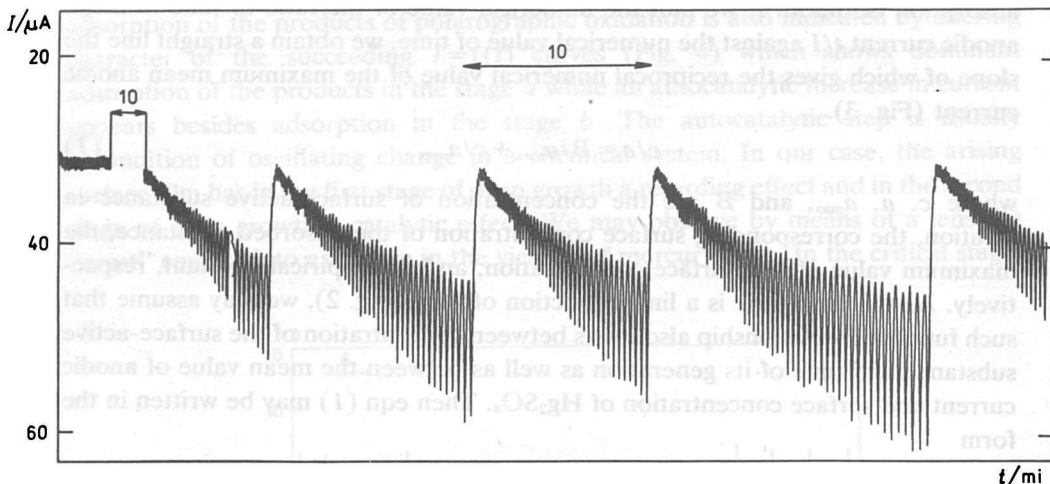


Fig. 1. Electrochemical oscillations of the system $\text{Hg}|\text{HSO}_4^-|\text{BrO}_3^-$. $c(\text{H}_2\text{SO}_4) = 2 \text{ mol dm}^{-3}$, $c(\text{NaBrO}_3) = 6 \times 10^{-2} \text{ mol dm}^{-3}$, $E = +0.04 \text{ V}$, $\theta = 20^\circ \text{C}$.

stability than it is in the case of homogeneous chemical oscillations, e.g. the Belousov—Zhabotinskii reaction. If the potential of dropping mercury electrode changes from $+0.06 \text{ V}$ to $+0.02 \text{ V}$, the mean value of oscillation period increases from 3 to 40 min.

The drop time increases linearly during a given oscillation period (Fig. 2) and the dependence of the mean anodic current on time shows character of the Langmuir

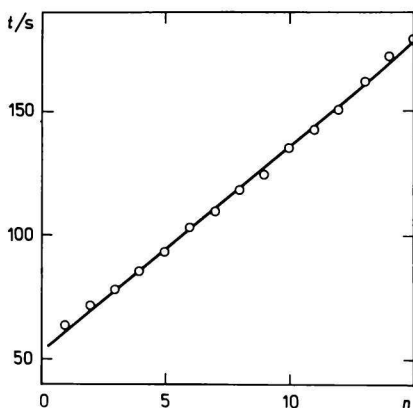


Fig. 2. Change of drop time of succeeding drops during an oscillation period.

n = drop number, $c(\text{H}_2\text{SO}_4) = 2 \text{ mol dm}^{-3}$, $c(\text{NaBrO}_3) = 5 \times 10^{-2} \text{ mol dm}^{-3}$, $E = +0.04 \text{ V}$, $\theta = 20^\circ \text{C}$.

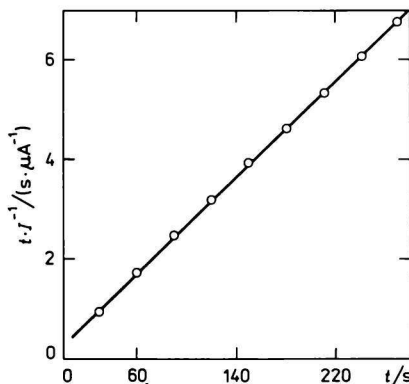


Fig. 3. Verification of the course of the Langmuir isotherm. $c(\text{H}_2\text{SO}_4) = 2 \text{ mol dm}^{-3}$, $c(\text{NaBrO}_3) = 4 \times 10^{-2} \text{ mol dm}^{-3}$, $E = +0.05 \text{ V}$, $\theta = 25^\circ \text{C}$.

adsorption isotherm. If we plot the numerical value of the ratio of time to mean anodic current t/I against the numerical value of time, we obtain a straight line the slope of which gives the reciprocal numerical value of the maximum mean anodic current (Fig. 3).

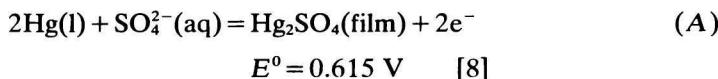
$$c/a = B/a_{\max} + c/a_{\max} \quad (1)$$

where c , a , a_{\max} , and B are the concentration of surface-active substance in solution, the corresponding surface concentration of the adsorbed substance, the maximum value of this surface concentration, and an empirical constant, respectively. As the drop time is a linear function of time (Fig. 2), we may assume that such functional relationship also exists between concentration of the surface-active substance and time of its generation as well as between the mean value of anodic current and surface concentration of Hg_2SO_4 . Then eqn (1) may be written in the form

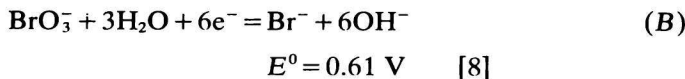
$$t/I = B'/I_1 + t/I_1 \quad (2)$$

where I_1 is the limiting value of the anodic current to which the measured courses correspond (Fig. 3).

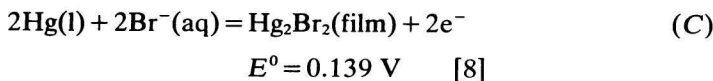
The periodical and oscillating course of the growth of mean anodic current and mercury surface tension are likely to be determined by the subsequent electrode reactions involving the formation of a surface film consisting of Hg_2SO_4 and, to a certain extent, Hg_2Br_2 . The anodic oxidation of mercury giving rise to the surface film of Hg_2SO_4 according to eqn (A) prevails at dropping mercury electrode in H_2SO_4 solution in the region of the above-mentioned potentials.



Provided the BrO_3^- ions are present in the solution, they are, to a certain degree, subject to electroreduction



yielding the Br^- ions. These ions are consumed in further electrooxidation of mercury



producing the surface film of Hg_2Br_2 .

The surface film consisting mainly of Hg_2SO_4 and, to a lower extent, Hg_2Br_2 evidently has a certain rate of electrocrystallization and is transferred at the orifice of dropping mercury electrode from drop to drop. A great and increasing

adsorption of the products of polarographic oxidation is also indicated by altering character of the succeeding $I=f(t)$ curves (Fig. 4) which shows dominant adsorption of the products in the stage *a* while an autocatalytic increase in current appears besides adsorption in the stage *b*. The autocatalytic step is usually a condition of oscillating change in a chemical system. In our case, the arising surface film has in the first stage of drop growth a retarding effect and in the second stage of drop growth a catalytic effect. We may observe by means of a lens the "crust" coming into existence in the vicinity of mercury drop. In the critical stage,

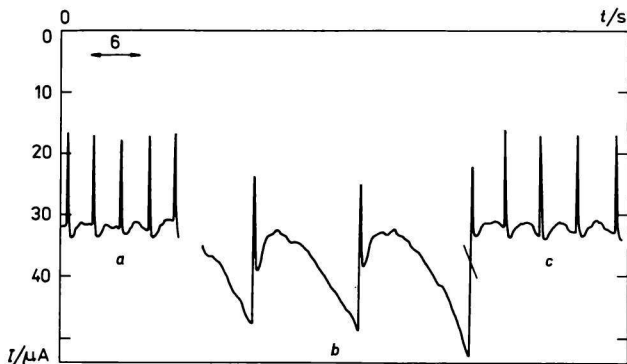


Fig. 4. Polarographic $I=f(t)$ curves. $c(\text{H}_2\text{SO}_4)=2 \text{ mol dm}^{-3}$, $c(\text{NaBrO}_3)=5 \times 10^{-2} \text{ mol dm}^{-3}$, $E = +0.04 \text{ V}$, $\theta = 25^\circ \text{C}$.

a) Start of oscillation period; *b*) end of oscillation period — region of limiting current; *c*) start of further oscillation period.

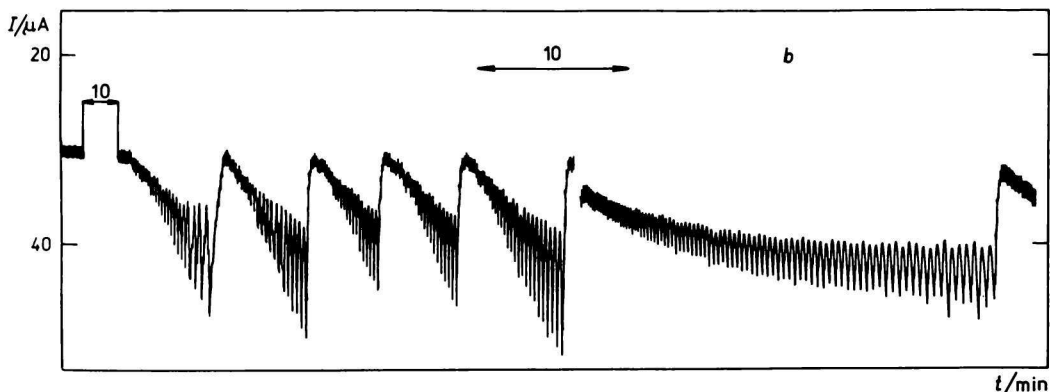


Fig. 5. Influence of gelatine on electrochemical oscillations of the system $\text{Hg}[\text{HSO}_4][\text{BrO}_3]$. For experimental conditions see Fig. 2.

a) Without gelatine; *b*) in the presence of 0.01 % of gelatine.

this "crust" breaks and the anodic current falls to the initial value. This process repeats itself during a few hours. The varying value of oscillation period may be due to unequal morphogenesis of the surface "crust" In the presence of 0.01 % of gelatine the average oscillation period considerably increases (Fig. 5), but the maximum value of anodic current decreases. The effect of gelatine obviously consists in its influence on texture of the surface film and thus on the rate of electrocrystallization.

As pointed out by Franck [9], the alternation of passivation and activation of electrode corresponds to positive feedback coupled with negative feedback. The described electrochemical oscillations may be a result of antagonistic interaction between the relatively rapid positive feedback and the slower negative feedback.

References

1. Nicolis, G. and Portnow, J., *J. Chem. Rev.* 73, 356 (1973).
2. Wojtowicz, J., in *Modern Aspects of Electrochemistry*, Vol. 8, pp. 47—120. (Bockris, J. O'M. and Conway, B. E., Editors.) Plenum Press, New York, 1973.
3. Gokhshtein, A. Ya. and Frumkin, A. N., *Dokl. Akad. Nauk SSSR* 132, 388 (1960).
4. Frumkin, A. N., Petrii, O. A., and Nikolaeva-Fedorovich, N. W., *Dokl. Akad. Nauk SSSR* 133, 1158 (1961).
5. De Levie, R., *J. Electroanal. Chem.* 25, 257 (1970).
6. Keizer, J., Rock, P. A., and Shu-Wai Lin, *J. Amer. Chem. Soc.* 101, 5637 (1979).
7. Dörfler, H. D. and Müller, E., *J. Electroanal. Chem.* 135, 37 (1982).
8. Sukhotina, A. M., *Spravochnik po elektrokhemii*, p. 134. Khimiya, Leningrad, 1981.
9. Franck, U. F., *Angew. Chem., Int. Ed. Engl.* 17, 1 (1978).

Translated by R. Domanský