STUDY OF AUTO-OSCILLATIONS IN PASSIVATION-FREE SYSTEMS USING A SOLID ELECTRODE

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As has been reported, periodic undamped current oscillations [1-3] have been observed in passivation-free electrolytic systems with a falling characteristic and their theory given [3]. So far these auto-oscillations have been investigated experimentally on stationary or growing mercury drop electrodes, and the results have been in complete agreement with theory. The theory does not associate the basic properties of auto-oscillations with any one form of electrode and only requires the epi-electrode layer to be renewed in some way or another for the system as a whole to be left in the quasi-stationary state. With the mercury electrode this is accomplished by the natural small-amplitude tangential oscillations of the mercury surface [1], which, without having any substantial effect on the distribution of concentration at the electrode surface, limit the thickness of the epi-electrode layer in which the principal change in concentration occurs before it reaches its value in the mass of the solution. A similar renewal mechanism can be produced on a cylindrical electrode executing circular vibrations. The problem of the present paper is to get a further check on the theory by eliminating the tangential oscillations and using some other way of renewing the epi-electrode layer. In the work done previously, an amalgamated rotating disc electrode* was used successfully [4] to take the stationary anion electro-reduction polarization curves. The rotating copper disc electrode used in the present work on auto-oscillations was not amalgamated, which made completely sure that spontaneous oscillations were absent from the surface, as required.

In accordance with the theory of [3], the form and properties of the periodic undamped auto-oscillations produced in this way (Fig. 1), are the same of those of the auto-oscillations found previously on a mercury drop electrode [1]. It follows from the theory [3] that if the oscillational process is going to go normally, the point where the system jumps from a state with large consumption of the substance used up at the electrode to a state with small consumption must be preceded by a state of affairs where the rate of consumption exceeds the rate of supply of the substance to the electrode surface. On the other hand, the jump from small consumption to large must be preceded by a state of affairs where the supply rate exceeds the consumption rate. The corresponding break points a and b (upper and lower break) are shown in Fig. 2 for a fixed voltage v, applied to the circuit. The circuit consists of an electrolyte with the electrode being polarized and an auxiliary electrolyte and the external resistance. The curves $i_a = c_a\bar{p}(\varphi)$ and $i_b = c_b\bar{p}(\varphi)$ give the relation between the currents i in the potential φ for values of the epi-electrode concentration existing in the states a and b of the system. The points a and b are where i_a and i_b are tangent to the straight line $ir+\varphi = v$. If v is reduced, the positions of the points a and b keep changing until they coincide with the point D, corresponding with the limiting position of the cycle of oscillations. The geometric positions of these points are given in Fig. 2 by the branches AD and BD. The curves $i_{01}(\varphi)$ and $i_{02}(\varphi)$ show how the stationary currents change with φ corresponding to the two thicknesses of the epi-electrode layer $l_2 < l_1$ with the constant concentration $\bar{c}$ in the body of the electrolyte (calculated from Eq. (3) of [3] for $G_1 = 0.14$, $G_2 = 0.20$, and $\bar{c} = 7$.

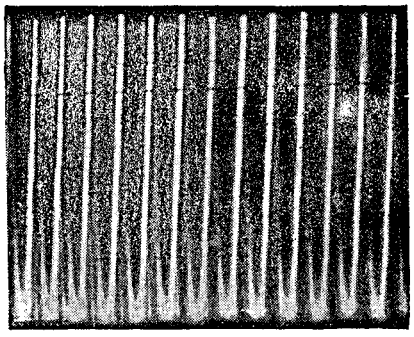

Fig. 1. Auto-oscillations of current at constant voltage. Rotating copper disc electrode in $6 \cdot 10^{-3}$ M $K_2S_2O_8$, $\omega = 15$ rps. Amplitude of oscillations $1.61 \cdot 10^{-4}$ amp, frequency 10 cycles per second.

* See also thesis by Yu. M. Povarov, Moscow University, 1958.

Let us see how the region Δv in which the auto-oscillations occur depends on l. The necessary condition given above in the case of l_1 reduces to the condition that the points a and b be located on different sides of the curve i_{01}. The limits of the region Δv_1 in which this condition is maintained are given by the values of v corresponding with the points of intersection of i_{01} and AD (left boundary) and with BD (right boundary). Similar reasoning determines the region Δv_2 for the other thickness of the layer l_2. Comparing the two results shows that the boundaries of the region Δv depend essentially on the thickness of epi-electrode layer.

This conclusion finds direct confirmation in the experimental results of Figs. 3a, b, c, d which give oscillograms of I vs. v taken at a small rate of reduction (from right to left) of the voltage, $v = 0.25$ v/sec, and different rates of rotation of the electrode ($\omega = 5, 8, 15, 29$ rps. respectively, increasing ω reduces l [5]). In accordance with theory, reducing the thickness of the epi-electrode layer is accompanied by a shift in the region Δv, so that those parts of the voltage axis leave it where the amplitude of the auto-oscillations is small (Fig. 3a–c). With further reduction in l, the region Δv degenerates (Fig. 3d). The single current jump in Fig. 3d is a transition caused by reduction in voltage where the system goes from one state to the other, followed by the system arriving at the stationary state.

Note that the region Δv as a function of l is essentially Δv as a function of the location of the curve of stationary states $i_0(\varphi)$, which is also determined by the concentration in bulk of the solution $\bar{c}$. Usually $\bar{c}$ remains constant in a series of experiments with different l. The way the region Δv varies with $\bar{c}$ at constant l and r may be found from the same considerations, if we bear in mind that i_0 increases proportionally with $\bar{c}$. The value of r is kept constant under these conditions by adding additional external resistance as the resistance of the electrolyte is decreased. Simultaneous changes in l and $\bar{c}$ can partially or (at large l) completely balance out their effect on Δv.

Because of the steepness of the brance AD, the displacement δv of the left boundary of the region Δv may be used to find the resistance of the system r (see Fig. 2). Here $r \cong \delta v / \delta I$ where δI is the change in stationary (limiting) current of the left boundary corresponding with the shift. Comparing the oscillograms of Figs. 3a and 3c gives $\delta v = 0.09$v, $\delta I = 40\mu$a and $r = 2.2 \cdot 10^3$ ohm. Let us calculate the resistance of the system in another way for comparison. In the present case (Figs. 1 and 3) no external resistance has been added, and r is determined by the resistance of the electrolyte in which the disc electrode of radius λ is immersed. It is not difficult to show by solving the corresponding boundary value problem that under limiting current conditions the voltage drops when the current passes through the electrolyte r at the center and at the edge of the disc are:

$$u(0) = \frac{i}{\sigma}\lambda, \quad u(\lambda) = \frac{2}{\pi}\frac{i}{\sigma}\lambda,$$

where σ is the specific conductance of the solution and i is the current density at the disc. Just as with the drop electrode, the disc electrode is not an equi-potential ($u(0)/u(\lambda) = \pi/2$), and so the resistance of the system is understood to be the value included between r_0 and r_λ, referred to the center and edge of the disc, $r_\rho = u(\rho)/I$. Since $I = \pi\lambda^2 i$,

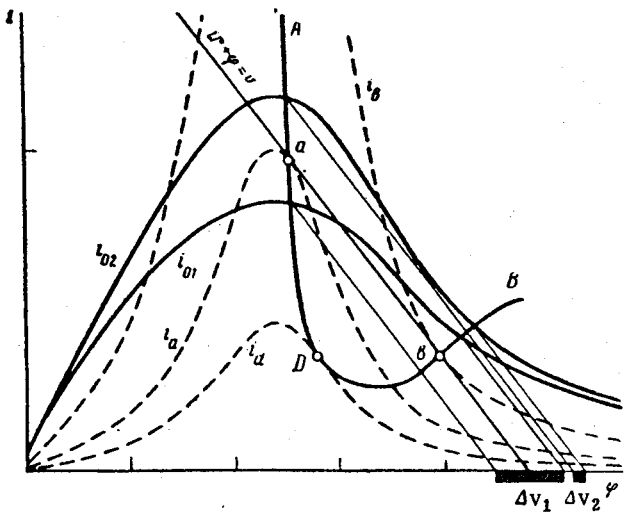

Fig. 2. Change in the auto-oscillation region with change in thickness of the epi-electrode layer.

$r_0 = 1/\pi\sigma\lambda$ and $r\lambda = 2/\pi^2\sigma\lambda$. For $3.7 \cdot 10^{-3}$ M $K_2S_2O_8$, $\sigma = 1.18 \cdot 10^{-3}$ ohm^{-1}cm^{-1}. Hence $r_0 = 2.7 \cdot 10^3$ ohm, and $r\lambda = 1.7 \cdot 10^3$ ohm. Thus, the condition is fulfilled that $r\lambda < r < r_0$, which supports the assumptions used above in calculating r.

We also find in accordance with the theory of [3] such facts (Fig. 3) as the constancy (at a fixed value of v) of the amplitude of the auto-oscillations with change in l and the reduction in period of the auto-oscillations of reducing the part of it where the current is small. If l is reduced there is an increase in the ratio ρ of that part of the period in which the current is large to the whole period. The exact derivation of the formula for the frequency (ν) of the auto-oscillations (which will be published shortly) shows that if v is fixed and l is reduced, ν does not change monotonically. It first increases, reaches a maximum at $\rho \approx 1/2$, and then drops to zero. The individual portions of this curve can be observed experimentally if the conditions are such that when l varies within the desired limits v stays in the region Δv (Δv as was shown above shifts with change in l). Under the experimental conditions of Fig. 3, the part of the curve was accessible to observation which corresponds with the values $\rho < 1/2$.

The geometrically inhomogeneous location of the different parts of the electrode surface in actual systems leads to the condition that the same stage of the process occurs in different parts of the electrode at somewhat different times. However, because of the mutual influence of different parts of the same electrode the time spread is not large,

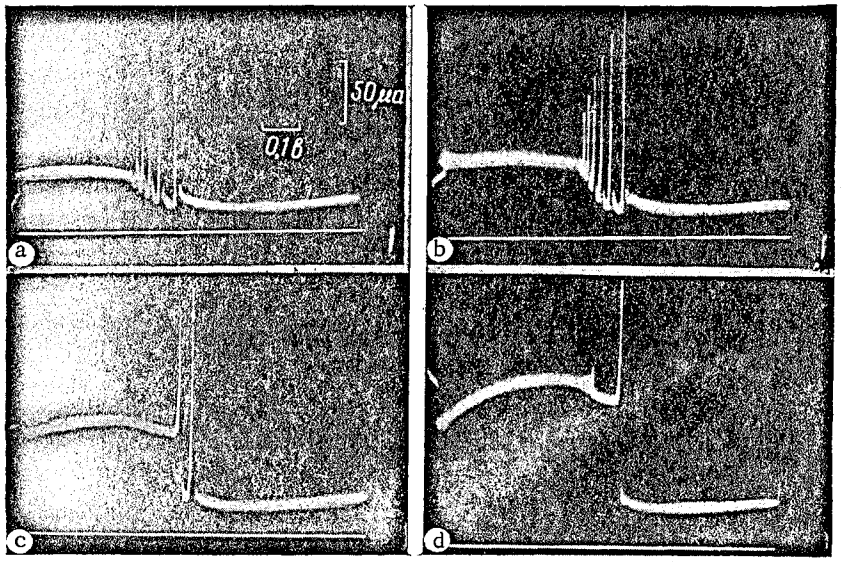

Fig. 3. Experimental study of auto-oscillations at different thicknesses of the epi-electrode layer. Rotating copper disc electrode, $2\lambda = 1.9$ mm, second electrode—platinum plate, $3.7 \cdot 10^{-3}$ M $K_2S_2O_8$ (the beginning of oscillogram b is shifted 0.04 v to the left of the others).

and cases of interference are only observed on the boundaries of the oscillation region. Differences in potential over the electrode caused by the inhomogeneity can be considerably reduced in those cases where it is permissible to add a considerable excess of extraneous electrolyte to the solution (systems with K_2PtCl_4, K_2PtCl_6 [4]).

An analysis of the results obtained from a study of auto-oscillations in passivation-free systems shows up a peculiarity in the behavior of electrolytic systems having a falling characteristic, mainly the possibility of very rapid transitions. An example is the transition from the state with small consumption of material to the state with large consumption (large rise in current at the front edge of the oscillations, Fig. 3). This is accelerated by the fact that the recharging of the electric double layer associated with the change in electrode potential occurs as a result of electro-reduction, the rate of which in a system with a falling characteristic increases as the potential is shifted to the positive side. Part of the negative electricity consumed in the electro-reduction flows away from the metal plate of the double layer, which takes on a more positive charge in accordance with the more positive potential of the electrode.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
