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On the Possibility of Determining Microquantities of Adsorbing Organic Compounds by an Oscillographic Method Using a Stepped Polarizing Voltage

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To increase the sensitivity of the polarographic method, preliminary accumulation of electrolysis products on the electrode is sometimes carried out. The methods of amalgam (1) and film (2) polarography are based on this principle. Recently a report appeared (3) on the use of anodic voltammetry with preliminary accumulation of the reduction product on a graphite electrode for determining methylene blue at concentrations of the order of $4 \cdot 10^{-5}$–$4 \cdot 10^{-9}$ mol/l.

In the present work another principle is proposed for increasing the sensitivity of polarographic determinations, based on adsorption of the molecules of the depolarizer itself on the electrode surface.

It is known that most organic compounds reduced at a mercury dropping electrode are capable of being adsorbed on it. The protonation of organic substances, which precedes the electron-transfer stage, as a rule occurs on the electrode surface (4). In this case the concentration of such substances on the electrode surface may exceed their concentration in the bulk of the solution many times over. Therefore, when a polarizing voltage is applied to the cell, the reduction current in the first moments of time should considerably exceed the value that would be obtained in the absence of adsorption. Use of the reduction current of a previously adsorbed compound makes it possible to change substantially the value of the minimum concentration being determined.

The possibility of practical implementation of such an experiment was shown in (5), using as examples the "first" oscillopolarographic curves $dE/dt = f(E)$ of semi- and thiosemicarbazones.

For the effective use of the adsorption phenomenon with the aim of increasing the sensitivity of the polarographic method, the following conditions are evidently necessary:

Fig. 1. Oscillopolarograms of thiosemicarbazone of acetoacetic ester.

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1. For substantial "enrichment" of the microelectrode surface with adsorbed molecules, sufficient time is required. Therefore, the microelectrode used here must be stationary.
2. Since the number of adsorbed molecules on the microelectrode surface is very limited, the polarogram must be recorded within a short time. Hence it is clear that, in order to obtain satisfactory results, oscillographic polarography must be used, the principal feature of which is the high rate of change of the polarizing voltage.
3. For determining small concentrations, highly sensitive apparatus is required. From this point of view, the most suitable is apparently an oscillographic polarograph with stepped polarizing voltage (6), which makes it possible to eliminate the charging current of the double-layer capacitance.

Experimental Part

The objects of the study were weakly acidic solutions of thiosemicarbazones of acetoacetic ester and methyl ethyl ketone at pH 4.6. A Britton–Robinson buffer was used as the background. Under these conditions the classical polarograms of the compounds had two waves, corresponding to the stepwise reduction of molecules of the substance that had been preliminarily protonated on the electrode surface, and also in the reaction layer near the electrode (5).

The polarographic cell used in this work, with a volume of 15 ml, was constructed as described in (7). As the microelectrode, the protruding amalgamated end of a platinum wire 0.25 mm in diameter and 0.2 mm long was used.

Fig. 1. Oscillopolarograms of thiosemicarbazone of acetoacetic ester. Initial polarizing voltage, −0.28 V; amplitude of the polarizing pulse, 0.8 V; pulse amplitude, 4 mV; rate of change of the polarizing voltage, 0.2 V/sec. Concentration (mol/l): a $-7\cdot 10^{-7}$, $-7.9\cdot 10^{-8}$, $-5.7\cdot 10^{-9}$, $-6.3\cdot 10^{-10}$. Instrument sensitivity (A/cm): a $-5.9\cdot 10^{-7}$, $-5.1\cdot 10^{-7}$, $-0.97\cdot 10^{-7}$, $-0.55\cdot 10^{-7}$.

A mercury drop with a surface area of 2.4 mm^2, obtained from a capillary placed in the same cell, was suspended on this electrode by means of a movable glass spoon. This design of the cell makes it possible rapidly to renew the stationary mercury microelectrode. Bottom mercury was used as the reference electrode.

The buffer solution placed in the cell was subjected to prolonged purging with nitrogen in order to remove dissolved oxygen. After this, to create the required concentration, a definite number of drops of the solution containing the substance under study was added to the cell with a calibrated pipette. Then, after renewal of the microelectrode, accumulation of the substance on its surface was carried out for one hour. During this process, nitrogen was again passed through the solution for stirring.

After completion of the accumulation process, a pulsed polarizing voltage of stepwise form was applied to the cell. The pause between individual pulses was 5 sec. The oscillopolarograms observed in this case are shown in Fig. 1.

Discussion of Results

It is evident from Fig. 1 that the method described makes it possible to determine very low concentrations of the substance under investigation. The polarogram of this substance contains two peaks (in some photographs the second peak is not noticeable because of its small size). It is characteristic that the diffusion loop observed on ordinary oscillographic polarograms is absent here. The polarographic peaks have a narrow, sharply descending shape. This feature is evidently common to oscillopolarograms obtained through the reduction of adsorbed molecules. It is explained by the considerable difference in the concentrations of the substance located on the surface of the microelectrode and in the bulk of the solution.

Curves of analogous form were obtained for a 10^{-5} M solution of thiosemicarbazone of methyl ethyl ketone. In this case the accumulation time was only 1 minute, and the polarographic cell used had the design described in work (8).

Figure 2 shows a plot of the dependence of the current magnitude at the peak of the first polarogram (see Fig. 2) on the concentration of the substance studied. Some deviations of this dependence from a linear law may be caused,

[Fig. 2 and Fig. 3 visible on page image]

Fig. 2

Fig. 2. Dependence of the current magnitude at the polarogram peak on the concentration of the substance. Accumulation time: 1 hour

Fig. 3

Fig. 3. Polarogram of a solution of thiosemicarbazone of acetoacetic ester. Amplitude of the polarizing impulse: 0.8 V. Initial voltages:
a–0 V, −+0.04 V, −+0.08 V, −+0.12 V, −+0.2 V

first, by the different adsorption rates for different concentrations of the substance; second, by depletion of the solution volume by adsorbing molecules; third, by partial hydrolysis of the substance studied. From the curves presented it is evident that the decrease in peak height occurs the faster, the lower the concentration of the substance in the bulk of the solution. After a certain number of polarizing impulses has been applied, the amount of adsorbed substance is depleted, and the surface of the microelectrode becomes contaminated with reaction products. As a result, on subsequent polarograms the current peaks for the reduction of the substance studied may disappear completely (for example, curve 3 in Fig. 1). Figure 3*a* shows a similar polarogram of a 10^5 M solution of thiosemicarbazone of acetoacetic ester, on which the reduction peaks of this substance are absent (the available

on the polarogram, the peak in the region of −0.13 V belongs to the background). Unlike the polarograms shown in Fig. 1, this polarogram is stable: its shape does not change with time during repeated recording. However, the picture changes if the initial level of the polarizing voltage is shifted into the positive region of potentials. From Fig. 3 - , which also shows stable polarograms, it is evident that a slight shift of the initial potential into the positive region leads to the appearance of reduction peaks of the substance under study with a characteristic shape. The reason for this is probably the interaction of mercury with the sulfur-containing compound, with formation on the electrode surface of a sparingly soluble complex (9), which is then reduced. On the control curves obtained at the same potential values in the absence of the substance under study, the above-mentioned characteristic peaks were not observed.

Thus, by setting a suitable initial polarizing voltage, it is possible to obtain a stable oscillopolarogram with well-defined peaks without preliminary accumulation.

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