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Timiryazev Institute of Plant Physiology, USSR Academy of Sciences

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OSCILLOGRAPHIC POLAROGRAPHY IN ORGANIC CHEMISTRY

G.K.Budnikov

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I. INTRODUCTION

The method of oscillographic polarography is based on the interpretation of curves obtained during the electrolysis of test solutions and recorded by a cathode-ray oscillograph. In ordinary or classical polarography the voltage applied to the polarographic electrolysis cell is varied according to a linear law, the rate of change of potential of the polarised electrode being deliberately selected at a low value of about 5 mV s^{-1} so that it has no influence on the shape of the polarogram. In oscillographic polarography the rates of change of potential vary from several millivolts to tens of volts per second. In some cases the rate of change of potential of the polarised electrode may reach several hundred volts per second. With a comparatively high rate of change of potential the current also changes rapidly, and a cathode-ray oscillograph is therefore used to measure the current; hence the name oscillographic polarography.

The methods of oscillographic polarography can be divided into two groups, depending on the form of the voltage applied to the polarographic cell. In the first group of methods, the voltage applied to the cell increases linearly. In the second group, it increases non-linearly, in particular sinusoidally.

The first papers on oscillographic polarography appeared about twenty years ago [1,2] and described chiefly the design and use of the instruments. Later, oscillographic polarography began to be employed as a highly sensitive analytical method. The most widely used methods have been those in which current–potential (i–E) curves are recorded with a voltage of triangular form applied to the cell, or in which curves for rate of change of potential as a function of potential, $dE/dt = f(E)$, are recorded with an applied voltage of sinusoidal form.

The general principles of oscillographic polarography and the theory of the method have been described in detail in a number of monographs [3-6] and reviews [7-12]. Oscillographic polarography is one of the newest instrumental methods of study, and is finding extensive application primarily in analytical chemistry. The value of the method is not restricted to analytical problems, however. Oscillographic polarography is widely used in organic chemistry, pharmacology [13-17], biochemistry [18,19], medicine [20,21], and oceanography [22]. In the present review an attempt is made to show how oscillographic polarography can be used to solve problems in theoretical organic chemistry. We shall deal chiefly with oscillographic polarography using alternating current, which gives $dE/dt = f(E)$ curves. This method is now the most fully developed with regard to both theory and apparatus. For comparison and comparative characterisation we shall give data from some work in which $i = f(E)$ curves were recorded.

II. PHYSICOCHEMICAL STUDIES BY OSCILLOGRAPHIC POLAROGRAPHY

For the sake of brevity we shall refer to the methods of oscillographic polarography in which the dependence of dE/dt on E and the dependence of i on E are recorded as the dE/dt method and the i–E method respectively.

The polarisable electrodes used in oscillographic polarography are the same as those used in classical polarography, *i.e.* the dropping mercury electrode, the hanging mercury drop [23-25], and solid electrodes [26]. In addition, jet electrodes are widely used in oscillographic polarography. Calomel electrodes, carbon electrodes, and the mercury macroelectrode are usually employed as reference electrodes.

To obtain oscillographic curves by the dE/dt method, an alternating current of about 0.5 mA with the dropping electrode and 5 mA with the jet electrode is passed through the polarographic cell. The mains are generally used as source of a.c. of frequency 50 c/s. [27]

In the absence of an electrochemically active substance, the $dE/dt = f(E)$ curve on an alkaline supporting electrolyte has an oval shape (Fig. 1). In the presence of a depolariser, the curve shows the appearance of incisions whose depth depends on the concentration of the depolariser and whose position along the potential axis depends on the nature of the depolariser.

The oscillogram for a solution containing a depolariser (Fig. 1) has two branches. The upper branch corresponds to the cathodic process and the lower branch to the anodic process. The extreme left-hand point of the curve corresponds to the dissolution potential of the mercury electrode, and the extreme right-hand point to the reduction potential of the cation of the base electrolyte.

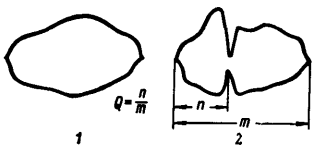


Fig.1. Oscillopolarographic $dE/dt = f(E)$ curves for:
1) 0.2 M NaOH solution;
2) 3×10^{-4} M benzil in the same solution.

Since several polarisation cycles take place during the lifetime of a single drop, a family of oscillograms can be obtained on the oscillograph screen for each drop. Therefore if a dropping mercury electrode is used, the oscillogram for the test solution is recorded in the last period of existence of the drop, when its surface is changing only slowly.

The theory of oscillographic polarography with a.c. is based on the general integral equation describing processes at a mercury electrode with polarisation by a current which changes as some function of time. Exact solution of this equation is possible only if we make certain assumptions, which are not, however, always experimentally justified. Kambara[28] and Madsuda[29] were the first to derive an equation for the oscillographic curve, but they made no allowance for the charging current in their calculations.

The form of the $dE/dt = f(E)$ curve was calculated approximately by Micka[30,31] for reversible processes, most of the factors determining the electrochemical process being taken into account.

The differential of the potential with respect to time in the potential range where neither dissolution of mercury (the extreme left-hand point on the $dE/dt = f(E)$ curve in Fig. 1) nor reduction of the cation of the base electrolyte (extreme right-hand point on the same curve) is reached is given by the expression

$$-\frac{dE}{dt} = \frac{i_0 \sqrt{\omega} \cos\alpha}{\frac{n_1^2 F^2 P_1}{RT(1+P_1)^2}(\sqrt{D_1}C_{1a} + \sqrt{D_2}C_{2a}) + C'\sqrt{\omega}}, \qquad (1)$$

where i_0 is the current density per square centimetre of the electrode surface, ω the angular velocity, $\alpha = \omega t$ + const = = the phase angle, n_1 the number of electrons taking part in the reduction of the substance, C' the specific differential capacity, D_1 and D_2 are the diffusion coefficients of reduced and oxidised forms of the depolariser, C_{1a} and C_{2a} the corresponding concentrations, R and T the usual thermodynamic constants, and P_1 is an exponential function:

$$\left(P_1 = \exp\frac{n_1 F}{RT}(E - E_1^{1/2})\right).$$

If we assume that the solution contains the depolariser exclusively in the oxidised form, *i.e.* that $C_{2a} = 0$, we find that the differential has a minimum value at the apex of the cathodic incision on the $dE/dt = f(E)$ curve. Calculations show that in the central potential range, from -0.5 to -1.5, where the incisions are most clearly defined, $\cos\alpha = 1$: *i.e.* the potential at the apex of the cathodic incision (and similarly the anodic incision) is equal to the half-wave potential of the depolariser.

The position of the incision on the potential axis is determined by the quantity Q, a quotient whose significance is apparent from Fig. 1. Other conditions being equal, the dimensionless quantity Q will naturally depend not only on the pH of the solution but also on the nature of the base electrolyte, since the latter determines the potentials at the extreme points on the curve. In the study of organic substances, Britton–Robinson buffer solutions and other buffer systems are usually employed. The potentials at the extreme points on the curve for these solutions (for a dropping mercury electrode) are found relative to a normal Weston cell and are used to determine the value of Q in volts. Table 1 gives potentials at the extreme points on the $dE/dt = f(E)$ curves for various buffer solutions.

An important feature is that the potential range in which the electrode is polarised is independent of the reference electrode used[8].

Close to the extreme points on the $dE/dt = f(E)$ curve, $\cos\alpha < 1$: *i.e.* the depth of the incision for a substance with a reduction potential which is either too positive or too negative is influenced by the steepness of the curve, which makes the incisions unsymmetrical and distorted with a reduced depth. In practice we usually deal with the relative depth h of the incision, which is equal to the ratio between the values of the derivative in the presence and in the absence of depolariser, and is defined as

$$h = \frac{KC}{KC + 4C'\sqrt{\omega}}, \qquad (2)$$

where C is the concentration of depolariser and $K = n^2F^2D^{\frac{1}{2}}/RT$.

From this it follows that the concentration dependence of the relative depth of the incision is hyperbolic, with one asymptote the horizontal axis. In practice this dependence is observed only approximately because of the various assumptions made in the calculation. Moreover, it follows from the formulae given above for the incision depth that the relative incision depth decreases only slightly with increase in the a.c. frequency, and this agrees with experiment.

In the absence of depolariser, *i.e.* when $C_{1a} = C_{2a} = 0$, the derivative is given by the expression

$$-\frac{dE}{dt} = \frac{i_0 \cos\alpha}{C'}, \qquad (3)$$

and for a given value of the current depends on the differential capacitance, which in turn depends on the electrode potential[32,33].

The dependence of differential capacitance on potential is characteristic of each electrolyte. Classical polarographic data can be used to estimate the magnitude of the

TABLE 1.

Polarographic support	E, V (s.c.e.)	
	left-hand point	right-hand point
1 M H_2SO_4	+0.41	−1.44
0.1 M HCl	+0.02	−1.47
Britton–Robinson buffers		
pH 1.81	+0.35	−1.50
pH 3.29	+0.29	−1.57
pH 4.10	+0.25	−1.61
pH 6.37	+0.18	−1.70
pH 7.96	+0.12	−1.75
pH 10.38	+0.07	−1.80
pH 11.98	+0.03	−1.84
0.1 M NH_4OH + 0.1 M NH_4Cl	−0.01	−1.92
0.1 M LiCl	+0.01	−2.20
0.2 M NaOH	−0.083	−1.96
0.2 M KOH	−0.080	−1.92

integral capacitance of the dropping mercury electrode[34]. For example, if the capacitance of such an electrode is 0.3 μF, the capacitive current for a rate of change of potential of 2 V s^{-1} is 6×10^{-7} A, which is no greater than the usual value in classical polarography. In the case of a.c. (*e.g.* 50 c/s), however, the rate of change of potential is large, and the capacitive current increases accordingly, reaching the same order of magnitude as the current produced by the electrochemical reaction. Thus oscillographic polarography makes it possible to study compounds which may not only react electrochemically at a polarisable electrode but also be adsorbed on its surface.

At a definite potential for each substance, an adsorption maximum is observed, reflected on the $dE/dt = f(E)$ curve by an incision of varying shape (sharp or in the form of an oval depression), often very similar to the depolariser incision. This phenomenon is observed in dilute electrolytes (*e.g.* 10^{-3} M sulphuric acid) and corresponds to the minimum in the differential capacitance of the mercury electrode at a definite potential. The nature of the incision can be determined by changing the a.c. frequency. If it is capacitive in character, its relative depth is insensitive to change in frequency.

Moreover, the depth of incisions due to capacitive phenomena decreases with increase in temperature, whereas the opposite relationship is observed for electrode processes involving electron transfer.

In order to determine whether the process recorded on the $dE/dt = f(E)$ curve is a capacitive process, it is necessary to compare the curve for the supporting electrolyte with the curve obtained after addition of a surface-active agent or a depolariser. In the potential range in which the substance is adsorbed on the electrode surface, the capacitance of the electrode decreases and, in accordance with Eqn. (3), the quantity dE/dt increases. This means that the $dE/dt = f(E)$ curve in this potential range goes beyond the limits of the supporting-electrolyte curve. In contrast, for processes involving electron transfer, as a result of the consumption of current in the reduction (or oxidation) of the depolariser, the curve at potentials more negative (or more positive) than the potential of the incision will lie inside the contour of the pure supporting electrolyte.

A characteristic feature of the oscillographic dE/dt method is that it permits separate observation of capacitive phenomena and processes involving electron transfer, whereas in the $i-E$ method, for example, the capacitive currents and oxidation or reduction currents are often superimposed on one another.

Although the dE/dt method also makes it possible to study the adsorption of organic substances on an electrode surface, the results obtained by this method are for the most part qualitative. The exact dependence of the differential capacitance on potential, characterising the adsorption of a substance, is determined by the method proposed by Frumkin[32].

To obtain a curve with clearly defined extreme points in the oscillographic dE/dt method (Fig. 1), use is made of a d.c. component superimposed on the a.c. component. The magnitude of this d.c. component is not fixed precisely, but depends on the composition and nature of the supporting electrolyte: it is always smaller with alkaline than with acidic solutions. The current density with which the electrode is polarised is given by the expression

$$i = i_0 \sin \omega t + i_1, \qquad (4)$$

where i_0 is the amplitude of the current density and i_1 the magnitude of the d.c. component (per square centimetre of electrode surface).

If i_1 is large, the electrode, being negatively charged, may acquire a potential equal to that at which the cation of the supporting electrolyte is reduced. In this case the $dE/dt = f(E)$ curve becomes a point. To obtain a curve of regular shape, the following theoretical relationship[30,35] should be satisfied

$$|i_1| < \tfrac{i_0}{2}\sqrt{\tfrac{T}{2t}},$$

where t is the drop time of the electrode and T the period of the a.c.

According to theoretical calculations, it is impossible to obtain a $dE/dt = f(E)$ curve of regular shape without superposition of a d.c. component if the current density is less than 0.02 A cm^{-2}. This is not always the case, however. This discrepancy is apparently due to the irreversibility of the electrode processes, *e.g.* by the deactivation of the reduction products of the supporting-electrolyte cation; this is shown to a particularly marked degree in solutions of strong acids. In general, there may be two causes of irreversibility: loss of reduction product of the support cation, or loss of the product of the anodic dissolution of mercury. According to the Nernst equation, in the first case there is a displacement of the electrode potential towards positive values; this displacement may be compensated for by a direct component which charges the electrode to negative potentials. The second factor brings about a displacement of potential in the opposite direction but is less marked than the first. The influence of the d.c. component on the shape of the oscillogram has been examined in more detail by Kalvoda[8] and Micka[30,31].

In oscillographic polarography the current passing through the polarographic cell is several times greater than the current in classical polarography. Thus in order to diminish the potential drop iR in the solution, it is necessary to use concentrated (1 M) supporting electrolytes. In the dE/dt method the potential drop is compensated for by a special assembly[36], which makes it possible to use, for the study of organic compounds, solutions with a high ohmic resistance (0.01 M electrolyte in the presence of an organic solvent).

In addition to the dE/dt method, there are other oscillographic methods, in particular the $i-E$ method. The appearance of the $i = f(E)$ curves depends on the form of the pulse applied to the cell. In the method which has now found widest use in organic oscillography, a triangular voltage pulse is applied to the cell. This method can be used to study both reducing and oxidising processes involving organic substances at an electrode. In the absence of electrochemically active compounds, the $i = f(E)$ curve has the form shown in Fig. 2 and, as in the case of the $dE/dt = f(E)$ curve, consists of two branches. If the solution contains a depolariser, the oscillogram shows peaks at potentials characteristic of the substance.

It has not yet been possible to obtain an analytical equation for the oscillographic $i = f(E)$ curve even for the simplest case, with allowance for only linear diffusion. Ševčik[37] obtained an equation by an approximate method, using the Laplace transformation. Randles[38] obtained a solution by a graphical method. Their solutions differ slightly from one another. Recently, Gokhshtein[39] has derived a general equation for reversible processes with cathodic and anodic polarisation.

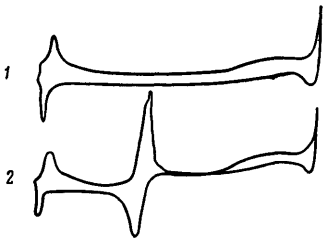


Fig.2. Oscillographic $i = f(E)$ curves for:
1) 0.2 M NaOH solution;
2) 3×10^{-4} M benzil in the same solution.

According to Delahay[6] the magnitude of the current i_p at the potential of the peak is given for reversible processes by the equation

$$i_p = 2.72 \times 10^5 n^{3/2} A D^{1/2} V^{1/2} C, \quad (5)$$

where A is the area of the cathode (in cm^2), D the diffusion coefficient, V the rate of change of potential ($V\ s^{-1}$), C the concentration of depolariser, and n the number of electrons taking part in the electrode reaction.

Unlike the case of the dE/dt method, the direct component of the current in the oscillographic $i-E$ method has a definite value, which influences the form of the resulting $i = f(E)$ curve. The presence in solution of surface-active substances which are adsorbed on the electrode is revealed on the $i = f(E)$ curves in the form of adsorption and desorption peaks, in contrast to the incisions on the $dE/dt = f(E)$ curves. The possibility of studying capacitive effects by the $i-E$ method has been discussed many times[40-42]. This question is discussed in more detail below.

The influence of atmospheric oxygen dissolved in the electrolyte in oscillographic polarography differs from that in ordinary polarography. To obtain the classical polarogram for a solution, preliminary removal of oxygen is necessary, but this is not essential in oscillographic polarography. This is of considerable value in the study of organic substances and reactions taking place at the moment of their dissolution.

III. USE OF OSCILLOGRAPHIC POLAROGRAPHY IN ORGANIC CHEMISTRY

Up to the present, the main attention in oscillographic polarography has been directed to the development of convenient analytical methods for the determination of various substances. It has been found that oscillographic polarography makes possible the quantitative determination of complex organic compounds such as the alkaloids of the tropane group[43-46] (cocaine, atropine, homatropine), the veratrine alkaloids[47], and a number of other alkaloids[48,49] and amino-acids[50] which cannot be determined quantitatively by classical polarography. Recently, however, oscillographic polarography has begun to be used not only for analytical purposes but also for the solution of various theoretical problems in organic chemistry. The number of substances which have been studied by oscillographic polarography is still small, so that systematic presentation of the results according to the classes of organic compound would not reveal clearly the advantage of oscillographic polarography in the study of organic substances. There are three fields in which oscillographic polarography is being used successfully for the study of organic substances — (1) study of the physicochemical properties of compounds, (2) study of the mechanism of electrode processes involving organic substances, and (3) study of chemical reactions and structural problems.

1. Study of Some Physicochemical Properties of Organic Compounds

In the previous Section it was shown that the adsorption of organic substances at an electrode–solution interface is revealed on the oscillographic curves in the form of incisions or peaks. The surface activity of a substance depends on its physicochemical properties, so that oscillographic polarography makes it possible to study certain physicochemical properties of organic compounds. The number of oscillographic studies devoted to this problem, however, is still small.

In the first experiments on oscillographic polarography, Heyrovský and his coworkers[51] found that distinct capacitive effects are given by substances which are sparingly soluble in the supporting electrolyte. Thus, alkaline solutions of pyridine and its homologues form adsorption films on a dropping mercury electrode; no adsorption is observed in the case of solutions in mineral acids. Aliphatic acids, on the other hand, are adsorbed on the electrode surface, giving capacitive effects on the oscillograms for acidic solutions. Their alkaline solutions are oscillographically inactive. Heyrovský and his coworkers found that adsorption films are formed by alcohols, phenyl salicylate, and camphor. Matiaš,[52] in a study of oscillographic $dE/dt = f(E)$ curves, also detected the adsorption of certain aliphatic alcohols and its influence on the reduction of cations. For each homologue studied, Matiaš found the potentials of adsorption and desorption at different concentrations in the solution.

The capacity effects produced by various alcohols on the $i = f(E)$ curves were studied by Loveland and Elving[53,54]. In the case of saturated solutions of pentanols, both branches of the oscillogram showed two peaks corresponding to adsorption and desorption of the alcohol molecules at the electrode surface. For n-hexanol, however, the authors observed three peaks on each branch, and for heptanol and octanol they observed four peaks. The same alcohols in the colloidal state gave two peaks on each branch of the oscillographic $i = f(E)$ curve. After removal of air from the colloidal solution, the oscillograms acquired the form characteristic of saturated solutions of the alcohols. On the basis of their results, Loveland and Elving concluded that mono- and bi-molecular films of the alcohols may be formed at the mercury–solution interface. The bimolecular film is revealed on the oscillogram by four adsorption and desorption peaks. With increase in the number of carbon atoms in the alcohol molecule, this tendency to form a bimolecular adsorbed film increases, and Loveland and Elving suggest that this is related to the solubility and dielectric properties of the alcohols in aqueous medium. The same authors[55], in a study of the adsorption of the eight isomeric pentanols, found that the difference between the potentials of the adsorption and desorption peaks appears to be related to the structure of the hydrocarbon radical of the alcohol molecule: the greater the degree of branching of this radical, the smaller the observed difference in the potential. From this it follows that the surface activity is determined by the chemical structure of the substance.

A detailed study of the adsorption characteristics of various aliphatic alcohols by the oscillographic dE/dt method has been made by Kalvoda[56]. Methanol and ethanol bring about only slight deformation of the curve for 1 M NaOH solution. With increase in the number of carbon atoms in the aliphatic alcohol molecule, however, the depth of the capacitive incisions increases (Fig. 3), and the capacity phenomena are observed at lower alcohol concentrations. The relative adsorbability of the individual alcohols was determined by means of two $dE/dt = f(E)$ curves for solutions with different concentrations of the alcohols being compared, for which the depth of the incisions was the same. The adsorption characteristics of aliphatic alcohols are compared with some of their physicochemical properties in Table 2. Kalvoda found that the slope of the straight line representing the potential of the capactive incision as a function of the logarithm of the concentration is determined by the nature of the alcohol molecule, and decreases with increase in the length of the aliphatic chain (Fig. 4).

It can be seen from Fig. 3 that adsorption may be revealed on the oscillographic $dE/dt = f(E)$ curves either as sharp incisions or as oval depressions on both cathodic and anodic branches of the curves. The shape of these incisions apparently depends on the rate of the adsorption process. In his study of the adsorption of aliphatic alcohols, Kalvoda[56] derived experimentally a simple rule, by means of which it is possible to distinguish a capacitive incision

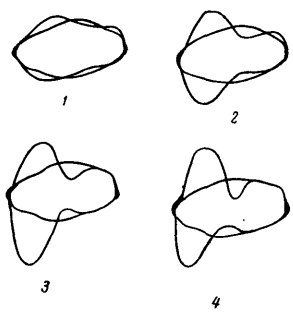


Fig. 3. Curves of $dE/dt = f(E)$ for alcoholic solutions:
1) 20% methanol in 0.8 M NaOH;
2) 20% ethanol in 0.8 M NaOH;
3) 0.5 M propanol in 1 M NaOH;
4) 0.008 M hexanol in 1 M NaOH.
The curves for the supporting electrolytes are given for comparison[56].

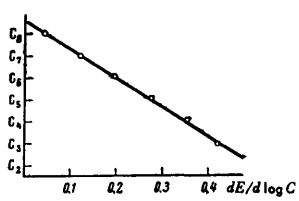


Fig. 4. Dependence of $dE/d\log C$ on the number of carbon atoms in the aliphatic radical of alcohols[56].

TABLE 2.

R	C_2H_5	n-C_3H_7	s-C_4H_9	iso-C_4H_9	n-C_4H_9	n-C_5H_{11}	n-C_6H_{13}	n-C_7H_{15}
Adsorption activity	1/1500	1/75	1/40	1/40	1/30	1/7	1	4
Concentration at which a detectable incision appears, M	1	$1.5 \cdot 10^{-1}$	$4 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$5 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$3.5 \cdot 10^{-4}$
Solubility of alcohol, g per 100 g H_2O	∞	∞	12.5	9.5	7.9	2.7	0.52	0.09
Boiling point, °C	78.3	97.2	99.5	108	117	138	155.8	174

from one corresponding to an electrochemical reaction in which electrons take part. With increase in the concentration of the substance studied to 0.01 M or 0.1 M, there will be no sudden break in the $dE/dt = f(E)$ curve at the potential of a capacitive incision. At the same time, the magnitude of the direct component of the current will have no influence on the shape of the incision, since in the case of capacitive processes no current is used up in electrolysis. In the case of incisions produced by electrolytic reduction or oxidation, however, increase in the concentration of the substance to 0.01 M causes a sudden break in the $dE/dt = f(E)$ curve at the potential of the incision, since further charging of the dropping electrode becomes impossible as all the electricity is used up in the electrochemical reaction. Kalvoda found that the depth of the capacitive incisions decreases with increase in the concentration of methanol in the solution. The presence of methanol in the solution has no appreciable influence on the depth of the electrochemical incisions.

Kalvoda[56] also studied the adsorption of a number of aromatic hydrocarbons and indole-3-carboxylic acids on a dropping mercury electrode.

Oscillographic polarography with triangular voltage pulses has been used by Gorokhovskii and coworkers[57,58] to investigate the relationship between the physicochemical properties of developers and stabilisers and their photographic action. They find that the appearance of symmetrical cathodic–anodic reversible peaks on the oscillograms for developers corresponds to high developing power. Addition of substances exhibiting a stabilising action in the photographic process produces little change in the capacity of the electrode.

2. Study of the Mechanism of Electrode Processes Involving Organic Substances

The use of oscillographic polarography to study the course of oxidation and reduction processes involving organic compounds is still in an early stage of development. The chief reason for this state of affairs is the difficulty and sometimes the impossibility of interpreting the oscillographic curves, since much work has been carried out under indefinite conditions in unbuffered solutions, and in most cases no comparison has been made between data obtained by oscillographic and classical methods. Only recently has a knowledge of the way in which the nature of a given electrode reaction is revealed on the oscillographic curves made it possible to apply oscillographic polarography to the study of the mechanism of electrochemical processes.

The shape of the oscillographic curve and the dependence of the position of each point on the curve, particularly of the incision or the peak, on the rate of change of potential

are functions of the type of process studied and its characteristic features. These features are related to the fact that the electrochemical process may depend on the diffusion of substance to the electrode or on a preceding chemical reaction or may be accompanied by adsorption. In turn, the processes accompanied by diffusion may be reversible, quasi-reversible, or irreversible. Having proposed the oscillographic method, Heyrovský [59] used it to study the reversibility of the reduction of a number of substances. The reversibility of an electrode process may be assessed from the relative positions of the incisions or peaks on the cathodic and anodic branches of the oscillogram.

It should be noted that the term "oscillographic reversibility" does not mean "polarographic reversibility". Usually, reversibility characterises the rapidity of a process studied by a definite method. In the case of "polarographic reversibility" the rapidity of a process is defined by the coincidence of the half-wave potentials of reduced and oxidised forms and by the shape of the polarographic wave. In the case of "oscillographic reversibility", however, the cathodic or anodic incisions or peaks should appear at identical potentials, and their shapes and depths should be approximately the same. If the potentials of the incisions or peaks are different or if one is completely absent, the process will be partly or completely irreversible. The basic difference between the concepts of reversibility of the electrode process in oscillography and polarography lies in the time required for reduced and oxidised forms of the substance to reach dynamic equilibrium with the electrode potential. In classical polarography the time required for dynamic equilibrium to be established in the electrode reaction is comparable with the drop time of the dropping mercury electrode ($\sim 2-3$ s). Since in oscillographic polarography the entire potential range over which the electrode is polarised is recorded on the screen in 0.01 s, while the electrode process takes $\sim 100-1000$ μs, in this case reversible processes must reach a state of equilibrium in an interval less than 1000 μs. Frequently a system which is reversible in classical polarography is irreversible in oscillographic polarography. There are also processes, however, which behave reversibly in oscillographic polarography but are irreversible in classical polarography. This anomalous behaviour is apparently due to the presence of consecutive electrochemical reactions. These reactions are unable to take place in the short polarisation times of the oscillographic method, but occur in classical polarographic reduction or oxidation, limiting the rapidity with which equilibrium is established. It may thus be said that the meaning of the concept "reversibility" depends on the method of investigation employed, so that the reversibility of a process can give us only approximate information on the rate at which equilibrium is established in the electrode reaction [60].

The number of known cases in which an electrode process controlled by diffusion is reversible is small (benzoquinone, nitrobenzene, etc.). Ševčik [37] showed mathematically that the potentials of the cathodic and anodic peaks of an oscillographically reversible redox system differ from the half-wave potential of the reversibly reduced or oxidised substance by $1.6RT/nF$ V, *i.e.* by $40/n$ mV. The method of oscillographic polarography with linear change in potential makes it possible to establish the nature of the process from the equation [41]

$$\log i_p = \log k + x \log v,$$

where k is the transfer coefficient, v the rate of change of potential, i_p the height of the peak on the oscillogram, and x the rate coefficient, which represents the dependence of the current at the peak on the rate of change of potential. For nitrobenzene $x = 0.5$. Reversible processes are characterised by a sharply defined peak on the oscillogram, but in the case of an irreversible electrode reaction, the peak is "flattened", and its maximum is less sharp. With irreversible processes, the peak height depends on the square root of the rate of application of the potential, giving a rate coefficient of 0.5. For a quasi-reversible electrode process this relationship is more complex, but under certain conditions, and within certain ranges of rate of change of potential, the rate coefficient is less than 0.5. An example of a quasi-reversible process is the reduction of pyrrole-2-aldehyde in dimethylformamide–water medium, for which Cappellina and Pederzini [61] found two peaks on the $i = f(E)$ curve. The position and the height of these peaks depended on the concentration of dimethylformamide in the solution; in the opinion of the authors, this was due either to differences in the solvation of pyrrole-2-aldehyde in dimethylformamide and in water or to a difference in the roles of the protons taking part in the reduction of the molecule. For both peaks the dependence of $\log i_p$ on $\log v$ was linear, and the rate coefficient varied over the range 0.25–0.44.

If the diffusion of depolariser is restricted by the rate of a chemical reaction preceding the electron-transfer stage, the depolariser being formed as a result of this chemical reaction from substances which are not reduced or are reduced at more negative potentials, the oscillographic $dE/dt = f(E)$ curve is L-shaped and the $i = f(E)$ curve is S-shaped (Fig. 5). The $i = f(E)$ oscillogram has no characteristic peak and resembles rather a classical polarogram (Fig. 5). To obtain a clearly defined incision on the $dE/dt = f(E)$ curve it is necessary to increase the concentration of the compound giving the kinetic incision by a factor of 100 relative to the concentration of substance whose electrode reaction is controlled by diffusion. For kinetic processes the rate coefficient is negligibly small: *i.e.* the peak height is almost independent of the rate of change of electrode potential. The temperature coefficient for a kinetic process is comparatively high. With increase in the frequency of the polarisation, the depth of the kinetic incision on the $dE/dt = f(E)$ curve decreases. A kinetic process can be distinguished from a diffusion-controlled process by the different effects of surface-active substances on the shape of this curve. An example is provided by the

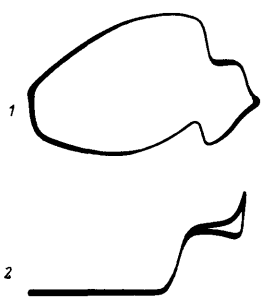


Fig. 5. Oscillograms for a 0.3 M solution of formaldehyde in 1 M NaOH:
1) $dE/dt = f(E)$ curve;
2) $i = f(E)$ curve.

behaviour of neutral solutions of maleic acid in the presence of gelatin. The first incision on the oscillogram corresponds to reduction of the undissociated acid molecule formed as a result of the recombination of an anion with a proton. This kinetic incision disappears after the addition of gelatin. The second incision corresponding to diffusion-controlled reduction of the maleic acid anion, is unaffected by the addition of gelatin[8]. In some cases the presence of surface-active substances (pyridine, alcohols) in solution may lead to retardation of the electrochemical process; this is revealed either by an increase in the difference between the potentials of the cathodic and anodic peaks or incisions (influence on reversibility) or by the splitting of one into several incisions (*e.g.* the influence of pyridine on the reduction of nitrobenzene in alkaline solution[34]). In general, adsorption films may decrease the rates of those electrochemical reactions which involve the transfer of two or more electrons[27].

We have seen above how capacitive effects are revealed on the oscillographic curves and how it is possible to distinguish an adsorption process from a process involving electron transfer. It should be added that a characteristic feature of the adsorption of a depolariser, revealed on the $i = f(E)$ curves, is that the rate coefficient at the peak is always greater than 0.5, but in general is less than 1, and that the peak height varies non-linearly with concentration of surface-active substance. The peak height–concentration curve resembles a Langmuir isotherm. The potential at which the saturation zone is reached, however, increases with rate of application of voltage to the polarographic cell[41].

An example of a catalytic process studied in detail by oscillographic polarography is Brdička's serological reaction[62].

The above characteristic features of electrode processes are used in the interpretation of oscillographic curves on which organic substances can in general give incisions and peaks of all types simultaneously. In oscillographic polarography, however, it is necessary to make allowance for one other important feature which is also the most frequent cause of discrepancy in the results obtained by classical and oscillographic polarography.

In polarography each drop grows at almost constant potential; the maximum change in the electrode potential amounts to ~ 20 mV in the lifetime of one drop. In this case a diffusion layer is formed only by the depolariser and the product of its electrode reaction. On separating from the capillary, the drop carries away the products of the electrode reaction, and the processes taking place on the fresh surface of the next drop are again those which correspond to the electrode potential and which cannot be influenced by the products of the reaction on the preceding drop.

In oscillographic polarography the electrode potential changes over a wide range (usually ~ 2 V) during the lifetime of one drop, and at a polarisation frequency of 50 c/s, for example, this change in electrode potential from 0 to 2 V is repeated 200 times. In the course of this rapid polarisation, the products of an electrode reaction taking place at a definite value of the potential are unable to diffuse into the depth of the solution and remain adjacent to the electrode, where they may either take part in an electrode reaction which takes place at a different potential or be converted chemically to another electrochemically active substance. Thus the oscillograms may show incisions or peaks corresponding to secondary processes involving intermediate compounds formed in the initial electrode reaction at the electrode surface. In classical polarography, the formation and nature of the intermediate compounds are determined from the shape of the waves and from the dependence of the half-wave potential on various factors.

The formation of these intermediate compounds, which are generally referred to as artefacts[63], is characteristic of oscillographic polarography, and in a number of cases has been demonstrated experimentally. The formation of artefacts may take place electrochemically in the course of the electrode reaction on polarisation of the electrode, or as a result of reaction of these intermediate products with one another, *i.e.* by a chemical process. Moreover, the artefacts may be substances produced at the electrode surface as a result of reaction of the intermediate compounds or certain components of the solution with mercury ions formed on positive polarisation of the electrode. These artefacts are reduced, giving corresponding incisions or peaks on the cathodic branches of the oscillographic curves. The polarograms in this case may show anodic waves corresponding to the formation of a compound containing mercury ions. An example is the formation of organomercury compounds with acetylene[64,65] and with certain ketones in alkaline solution[63].

The artefacts may reveal themselves in various ways — by being oxidised, by being reduced, or by being adsorbed on the electrode surface and changing its capacitance. In order to reach unambiguous conclusions in the examination of oscillographic curves, it is necessary to use results obtained by other methods. First of all the results obtained by oscillographic polarography must be compared with those obtained by classical polarography: incisions or peaks on the oscillograms not corresponding to polarographic waves are produced either by adsorption or by artefacts.

If the electrochemical reaction is reversible, the incision or peak of the artefact lies on the opposite branch of the oscillogram at the same potential as the incision or peak of the original depolariser. The oscillogram does not, however, tell us whether the depolariser in solution is in the oxidised form and the artefact on the electrode surface in the reduced form, or *vice versa*; nor does it give the percentages of the depolariser present in the solution in the reduced and oxidised forms. In this case also it is necessary to use data obtained by classical polarography. If two incisions or peaks on an oscillogram lie opposite one another at the same potential on the two branches of the curve, we may again be dealing with two different, independent processes, particularly when the shapes of the incisions or peaks differ.

To identify an intermediate compound taking part in the formation of a redox system, it is possible to use the polarographic method with Kalousek's switch[66-68]. In this method we apply to the dropping mercury electrode a definite auxiliary potential at which the test substance gives the limiting diffusion current, after which the electrode is alternately switched, at a definite frequency, out of this auxiliary circuit and into the polarograph. For example, if the compound is reduced reversibly at a dropping mercury electrode, Kalousek's switch can be used to obtain the anodic wave for the oxidation of the resulting intermediate compound at the same potential. An advantage of this method is that the frequency used in this case is lower than that of the ordinary oscillographic method based on the use of a.c. This simplifies considerably the instrumentation of the method. It has recently been shown[68] that, in work

with this switch, it is necessary to make allowance for the charging currents, which in this case reach higher values than in ordinary polarography, and depend on the auxiliary potential. If the compound being studied is adsorbed on the electrode surface, it is possible, by applying an auxiliary potential at which almost complete desorption of the substance takes place (*e.g.* -2 V), to record its adsorption wave at the potential of its adsorption. The height of this wave will depend both on the auxiliary potential and on the frequency of switching (Fig. 6). This method will probably find further application in the interpretation of oscillograms and the study of the adsorption of organic substances.

To identify the artefacts formed in the course of irreversible electrochemical reactions, it is necessary to follow the influence of the d.c. component on the shape of the oscillographic curve. If by varying the d.c. component we polarise the electrode in such a way that its potential does not reach the value at which the primary electrode reaction takes place, the incision or peak corresponding to the artefact will disappear, since in this case no intermediate product will be formed at the electrode. To investigate the nature of the artefact, it is also necessary to study the influence of the composition of the support and the concentration of the base electrolyte on the shape of the oscillogram. With a change in the support composition, it is possible, by adding a polarographically active electrolyte in excess, to determine the potential range in which formation of the artefact takes place and also to determine which of the support components is involved. For example, carbon disulphide gives incisions on the $dE/dt = f(E)$ curve at positive potentials only when the electrode potential reaches -2 V. When the solution contains an excess of zinc ions (concentration > 0.01 M), the CS_2 incisions disappear, since the electrode potential in this case[8,63] is slightly greater than -1 V, so that reduction of carbon disulphide with the formation of S^{2+} ions, which is responsible for the appearance of incisions at positive potentials, does not take place. Analogous phenomena have also been observed in the case of penicillin[8].

Valuable information on the mechanism of an electrode reaction can be obtained by means of the so-called "first curves".[69,70] These curves indicate whether the artefacts are formed after the first cycle or during repetition of the polarisation cycles. The capacitive incisions are often more clearly defined on the first curves than on the multiwave oscillogram. Kalvoda[56] has observed a similar phenomenon for aliphatic alcohols. If capacitive effects are excluded, the first curves obtained by the oscillographic method with a.c. correspond most closely to the polarographic waves, since artefacts are not revealed on these curves. The concept of "first curves" in this sense naturally relates only to the cathodic branch of the oscillogram.

The use of a jet electrode may be extremely valuable in the study of electrochemical processes involving organic substances. Recently, an electrode of original design has been developed with which the surface area of the jet is independent of the quantity of solution studied[71]. With the rapid renewal of the surface of the jet electrode, products of the electrochemical reaction are unable to concentrate in the layer next to the electrode and interact to form artefacts, so that the oscillographic curves obtained with a jet electrode generally have a simpler shape than the curves obtained for the same solution with a dropping electrode. The jet electrode may reveal only very readily formed artefacts such as organomercury compounds.

In cases in which the products of the electrode reaction may exert a retarding influence on the primary electrochemical process, the incisions corresponding to the primary process are more clearly defined on the curves obtained with a jet electrode than on the curves recorded at a dropping mercury electrode. For example, the incisions corresponding to the reduction of carbon disulphide are hardly detectable on the oscillograms obtained at a dropping electrode. In the case of the jet electrode, these incisions are much more clearly defined, the cathodic incision for the artefact being almost non-existent (Fig. 7).

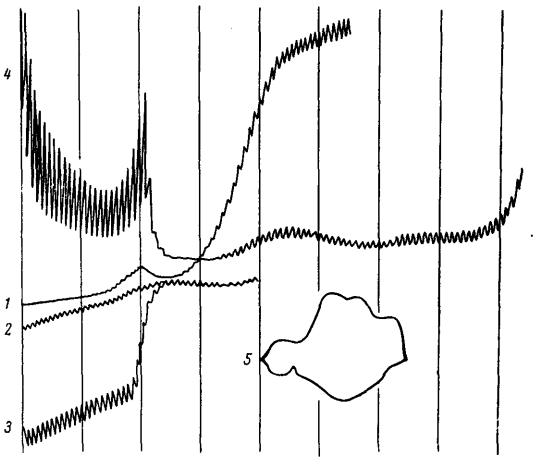


Fig. 6. Curves for a 10^{-4} M solution of tetraphenylethylene glycol in 50% methanol, 0.5 M H_2SO_4; origin of curves 0.0 V; 200 mV along the abscissa; Yanagimoto PA-101 polarograph (1960); sulphate reference electrode:
1) classical polarogram;
2) polarogram recorded by means of a Kalousek switch, auxiliary potential -0.6 V;
3) the same curve for a potential of -1.2 V;
4) a.c. polarogram;
5) oscillographic $dE/dt = f(E)$ curve.

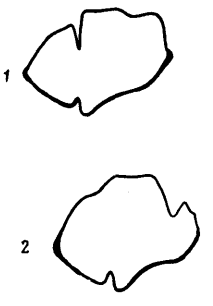
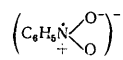


Fig. 7. Oscillographic $dE/dt = f(E)$ curves for a 5×10^{-4} M solution of carbon disulphide in acetate buffer at:
1) dropping mercury electrode;
2) jet electrode[8].

If intermediate compounds are formed in sufficient quantity during the electrode reaction, they can be detected by means of a mercury electrode with a small surface area, such as the hanging drop[23-25], and the curves can be recorded by the usual polarographic method.

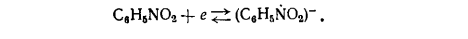
A typical example of a reaction involving the formation of various intermediate compounds is the reduction of nitrobenzene[72], whose electrochemical behaviour has been studied by many workers. Nitrobenzene was used in the first oscillopolarographic measurements by Heyrovský[3,5]. From the depth of the cathodic incision on the oscillographic curve for nitrobenzene in alkaline solution it was calculated that its electrolytic reduction is a four-electron process. When a surface-active substance, *e.g.* pyridine, is added to a solution of nitrobenzene, the four-electron incision for nitrobenzene is split into two. Of the resulting cathodic incisions, the first corresponds to a one-electron reduction, and the second to a three-electron process. The sum of the areas of the two incisions is equal to the area of the initial four-electron incision. Thus the four-electron reduction of nitrobenzene in alkaline solution in the presence of a surface-active substance takes place in stages: the molecule first takes up an electron to form a radical-anion



which is reduced to the hydroxylamine derivative only at more negative potentials. It should be noted that nitromethane under the conditions of oscillographic polarography is reduced according to a four-electron mechanism[5]. The incision for nitrobenzene is much sharper than that for nitromethane, however, and from this it was concluded that the nitromethane molecule adds on four electrons successively, not rapidly and simultaneously as in the case of the nitrobenzene molecule. Kemula and Kublik attempted to follow the formation of artefacts during the reduction of nitrobenzene by using the method of cyclic voltammetry with a hanging mercury drop[24]. This method, as proposed by Kemula and his coworkers and by Vogel[25], is essentially analogous to oscillographic polarography with a low rate of application of potential of symmetrical sawtooth form. It is of interest that Delahay[6] classifies oscillographic polarography in which $i = f(E)$ curves are studied as a method of multiwave voltammetry with continuously changing potential. Thus by means of cyclic voltammetry it is possible to change from classical polarography to oscillographic polarography and conversely; this is of particular importance in the study of the mechanism of electrochemical processes involving organic compounds.

In Kemula and Vogel's method, using a hanging mercury drop as electrode, the products of the primary electrode process and of secondary reactions remain close to the electrode and may be determined. An analogy is also observed in the case of preparative electrolysis at a mercury microelectrode. An advantage of the hanging drop compared with the latter method is that the products of the electrode reaction can be studied directly, in the same solution and at the same electrode.

During polarographic reduction, nitrobenzene is converted into phenylhydroxylamine. During polarisation of the hanging drop in cyclic voltammetry, the nitro-group is likewise reduced to the hydroxyamino-group at the surface of the microelectrode. During the reverse polarisation, the phenylhydroxylamine formed is oxidised on the electrode surface to nitrosobenzene at -0.22 V (relative to the saturated calomel electrode, s.c.e.). In the second cycle, nitrosobenzene is reduced to phenylhydroxylamine. Kemula and Kublik[23] found that the redox potential of the reversible nitrosobenzene–phenylhydroxylamine system is displaced to more negative values with increase in the pH of the solution. In strongly alkaline solutions, nitrosobenzene reacts with phenylhydroxylamine to form azoxybenzene; the peak corresponding to reduction of the nitroso-group disappears, and the peak corresponding to reduction of the nitro-group forms an inflection. In Kemula and Kublik's opinion this inflection is due to the influence of the resulting surface-active substance, azoxybenzene; this was confirmed by analysis of the cyclic-voltammetric curves for a mixture of azoxybenzene and nitrobenzene. In this case a new reversible redox system is produced:



If during polarisation of the electrode the potential does not reach the value at which reduction of the nitro-group takes place, the nitrobenzene–phenylhydroxylamine system is not formed. Kemula and Kublik also tried to explain the nature of some of the incisions on the $dE/dt = f(E)$ oscillographic polarograms for nitrobenzene solutions. They attributed the decrease in the depth of the incisions corresponding to the nitrobenzene–phenylhydroxylamine system with increase in the direct component of the current to a change in the mechanism of reduction of the nitro-group. If the electrode polarisation reached -2.0 V, the nitrobenzene is reduced to aniline, as a result of which the incision for phenylhydroxylamine and hence nitrobenzene decreases. With increase in the pH of the solution the $dE/dt = f(E)$ curves showed new incisions, whose nature could not be determined.

The oscillogram for an alkaline solution of nitrobenzene is very complex (Fig. 8). Of the six incisions on the curve, only one corresponds to the polarographic wave for nitrobenzene; the other incisions correspond to various intermediate compounds.

Volke[73] made a detailed study of the oscillopolarographic behaviour of nitrobenzene over a wide pH range in order to compare data on the reduction of nitrobenzene with data obtained in an oscillographic study of isomeric nitropyridines[74], which also, like nitrobenzene, gave complex

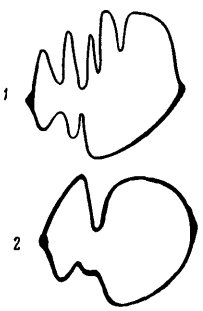


Fig. 8. Curves of $dE/dt = f(E)$ for a 10^{-3} M solution of nitrobenzene in 1 M KOH at:
1) dropping electrode;
2) jet electrode[34].

curves. He showed in the case of nitrobenzene how oscillographic polarography can be used to study the mechanism of an electrochemical reduction and to identify the intermediate products and the sequence of their reactions with one another.

Since the products formed during the electrolytic reduction of nitrobenzene are known, Volke first of all studied the oscillopolarographic behaviour of these compounds and determined the potentials of their incisions. The nitrobenzene–phenylhydroxylamine system was studied. In contrast to the polarographic results, the oscillographic $dE/dt = f(E)$ curve in the potential range where polarographic reduction of phenylhydroxylamine takes place showed no clearly defined incision; the presence of an anodic incision on the curve indicated that the phenylhydroxylamine is oxidised at the dropping mercury electrode. The oscillograms for alkaline solutions of phenylhydroxylamine were complex and very similar to the curves for nitrobenzene under the same conditions (Fig. 8). It was found that the shape of the curves changed with time; the depth of the incision for the nitrobenzene–phenylhydroxylamine redox system changed particularly rapidly in the presence of atmospheric oxygen, and new incisions appeared. In the case of a jet electrode, the curve for phenylhydroxylamine in alkaline solution was again complex, indicating that chemical changes take place in the phenylhydroxylamine solution. Volke also found that at pH < 2 the azobenzene–hydrazobenzene redox system is reversible; this was confirmed by polarography with a Kalousek switch. Azoxybenzene shows irreversible behaviour during electrolytic reduction; the number of incisions on the oscillogram depends on the concentration of depolariser. On the basis of a study of the first curves for azoxybenzene, Volke concluded that, as in classical polarography, azoxybenzene was first reduced with the attachment of four electrons, and four protons to form hydrazobenzene, which gave capacitive effects on the curves. During the reverse polarisation in the first cycle, hydrazobenzene was oxidised, with the participation of two electrons, to azobenzene, which in the second and subsequent cycles was reduced to hydrazobenzene and gave a corresponding incision.

$$C_6H_5-\underset{\underset{O}{\downarrow}}{N}=N-C_6H_5+4e+4H^+ \longrightarrow C_6H_5-NH-NH-C_6H_5+H_2O,$$

$$C_6H_5-NH-NH-C_6H_5 \longrightarrow C_6H_5-N=N-C_6H_5+2e+2H^+,$$

$$C_6H_5-N=N-C_6H_5+2e+2H^+ \longrightarrow C_6H_5-NH-NH-C_6H_5.$$

Detailed study of the oscillopolarographic behaviour of these redox systems enabled Volke to explain the complex curves for nitrobenzene. According to the polarographic data, the electrochemical reduction of nitrobenzene in acidic and neutral solutions takes place in an essentially simple fashion and is represented by the following scheme:

$$C_6H_5NO_2+4e+4H^+ \longrightarrow C_6H_5-NHOH+H_2O,$$

$$C_6H_5NHOH \rightleftarrows C_6H_5NO+2e+2H^+.$$

This is confirmed by data on the effect on the depth of the incisions of adding the corresponding intermediate compounds, by the first curves, by the influence of the d.c. component on the shape of the oscillogram, and by the curves obtained with a jet electrode.

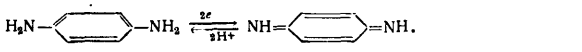
With increase in the pH of the solution there is an increase in the rate of the reaction between phenylhydroxylamine and the nitrosobenzene which is formed as an artefact at the electrode surface, with the production of azoxybenzene:

$$C_6H_5NHOH+C_6H_5NO \longrightarrow C_6H_5-\underset{\underset{O}{\downarrow}}{N}=N-C_6H_5+H_2O.$$

Thus identification of the incisions on the curves for nitrobenzene enabled Volke to explain its electrochemical behaviour. Like Kemula and Kublik[23], Volke found that azoxybenzene influenced the reduction of nitrobenzene and assumed that the latter forms the polarographically active $C_6H_5\dot{N}O_2^-$ radical in the presence of azoxybenzene.

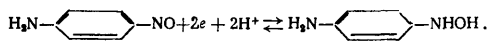
Our study[75] of the oscillopolarographic behaviour of the semicarbazones and thiosemicarbazones of isomeric nitrobenzaldehydes has shown the marked similarity between the behaviour of the nitro-group in these compounds and in nitropyridines and nitrobenzene[73,74]. The nitro-group in these semicarbazones and thiosemicarbazones is apparently reduced by a mechanism similar to that for nitrobenzene.

By means of cyclic voltammetry with a hanging mercury drop, Kemula and Kublik[24] detected the formation of a number of intermediate products in the reduction of *p*-nitroaniline in 0.1 M potassium hydroxide solution. In the first drop-polarisation cycle, *p*-nitroaniline is reduced to *p*-phenylenediamine, which is then oxidised on the electrode surface to *p*-benzoquinonediimine and gives the corresponding oxidation peak at the end of the cycle. Reduction of the diimine takes place in the second cycle, this redox system being reversible.

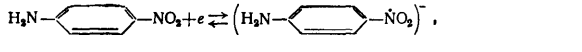


These conclusions were confirmed in a study, under the same conditions, of *p*-phenylenediamine, whose oscillograms showed peaks identical to the positive peaks for *p*-nitroaniline on the cyclic-voltammetric curves. Later, Olson *et al.*[76] obtained similar results using a graphite paste electrode instead of a hanging mercury drop.

Of the five incisions on the $dE/dt = f(E)$ curve for *p*-nitroaniline, only three correspond to the three peaks on the cyclic-voltammetric curve for this substance. Kemula and Kublik[24] suggested that the additional pair of incisions on the oscillogram belong to a new redox system formed under the conditions of oscillographic polarography:



Addition of camphor, which brings about splitting of the wave for *p*-nitroaniline in alkaline medium, leads to the appearance of a second peak on Kemula's cyclic curve, apparently owing to the formation of a reversible redox system at -0.8 V (s.c.e.)



similar to the system produced in the case of unsubstituted nitrobenzene under the same conditions.

In the cases examined, the artefacts formed under oscillographic conditions took part in various reactions involving electron transfer and thus revealed themselves on the oscillograms. The substances and artefacts studied may, however, give various capacitive effects on the oscillographic curves, being adsorbed on the electrode surface.

In the study of these capacitive phenomena, a marked analogy may be observed between the oscillographic curves for the substances studied and their a.c. polarograms, or as they are still called, tensametric curves. This method of polarography with a.c. was first proposed by Frumkin[77] and used to study adsorption phenomena at a dropping mercury electrode. The method consists in measurement of an alternating current which passes through the cell and depends on the electrode potential, the latter being altered in the usual polarographic manner.

The a.c. polarogram resembles a differential polarogram, but whereas on the latter a maximum corresponds to a definite electrode reaction involving reduction of a component of the solution being studied, the position of a maximum on the a.c. polarogram is determined not only by this reaction but also by capacitive phenomena at the electrode surface–solution interface. If no reduction process takes place at the electrode, a so-called tensametric curve is obtained, analogous to a capacitance–potential curve[78]. Recently, a.c. polarography has been widely used, chiefly in organic polarography. The general principles of this method have been described in a number of papers[6,78,79]. The a.c. polarogram often corresponds more or less exactly to the oscillographic curve, and hence makes it possible to interpret the latter. Curves obtained by different methods for phenyl trityl ketone (Fig. 6) show that this compound is first adsorbed on the surface of the dropping electrode, after which the adsorbed form is reduced, and the product is desorbed from the electrode surface.

The intermediate compounds formed during the rapid and repeated polarisation of the electrode complicate interpretation of the oscillograms; the use of a jet electrode instead of a dropping electrode in oscillographic polarography has therefore been recently recommended. However, the possibility of recording oxidation and reduction reactions in rapid succession and of identifying the resulting intermediate compounds means that in the near future oscillographic polarography with a dropping electrode will become an effective method of studying the mechanism of electrochemical processes involving organic substances. In this connection oscillographic polarography may be of considerable assistance in the industrial electrolytic synthesis of organic compounds. One example is of interest. It has previously been pointed out[80,81] that the electrochemical reduction of acetone, ethyl methyl ketone, phenylacetone, acetophenone, cyclopentanone, cyclohexanone, and benzaldehyde at a mercury cathode is accompanied by formation of the corresponding organomercury compounds. These compounds were isolated from solution when reduction was complete.

In a review of work on the oscillographic polarography of ketones, Kalvoda[82] drew attention to the anodic incisions at positive potentials on the oscillographic $dE/dt = f(E)$ curves for a number of carbonyl compounds, particularly acetone and cyclohexanone. These incisions are observed only with acidic solutions of ketones; they become smaller with increase in the pH of the solution, and are almost non-existent at pH ~ 3.0. The anodic incisions for ketones appear only when the negative potential of the electrode exceeds -1.3 V, *i.e.* when hydrogen is liberated. Thus the curve, for a sulphuric-acid solution of acetone, recorded with a hanging drop and reverse polarisation of the electrode from -0.3 V, contains no peaks. When a potential of -1.5 V is applied to the electrode for 20–25 s, however, the same curve shows a deep peak corresponding to oxidation of the resulting product at a potential of about 0 V. With decrease in the d.c. component, the anodic incisions for the ketones disappear. Hence it is concluded that the anodic incisions for acetone correspond to artefacts formed at negative potentials. Known products of the reduction of acetone, such as pinacol, isopropanol, and propene, do not give anodic incisions on the corresponding oscillograms; but the product which is isolated during the preparative electrolysis of acetone at a mercury cathode and which contains an organomercury compound, probably diisopropylmercury, gives analogous anodic incisions. In the preparative reduction of cyclohexanone at a mercury cathode, Kalvoda isolated dicyclohexylmercury, which also gave anodic incisions analogous to those on the curve for a sulphuric acid solution of cyclohexanone. It has thus been shown that the reduction of certain carbonyl compounds at a mercury electrode involves the formation of an artefact in which the surface of the electrode itself participates. The mechanism of this process is not yet clear.

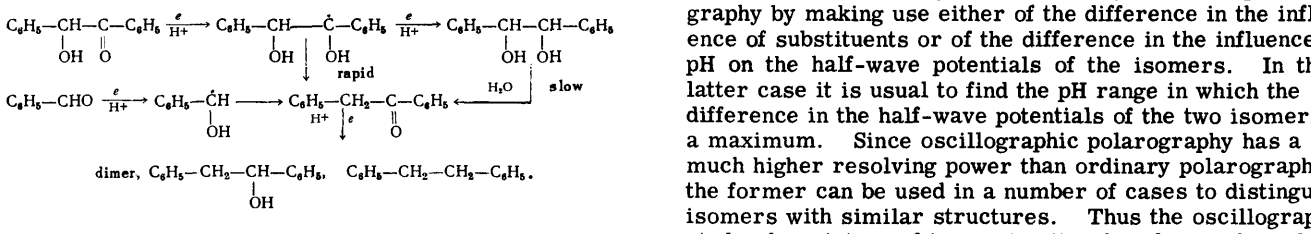
In a study of benzaldehyde in buffer solutions by the oscillographic $i-E$ method, Valenta[83] also detected anodic peaks at positive potentials on the oscillograms. In this case also the anodic peak is apparently due to oxidation of an organomercury compound formed at negative potentials.

The following analogy can be drawn between oscillographic polarography with a.c. and macroelectrolysis used for preparative purposes. In the preparative electrolysis of organic compounds on the industrial scale, electrolytic reduction with controlled current is most frequently used. Electrolysis in this case takes place either at the reduction potential of the substance or at the deposition potential of the cation of the supporting electrolyte. The yield of product, however, depends on a number of factors (electrode material, current density, temperature, composition of solution, etc.). In general, electrolysis in this case gives several substances, some of which are side-products. A somewhat analogous phenomenon is observed during the reduction of a substance under conditions of oscillographic polarography, since the product formed at one potential may react further at the electrode at a different potential. Under the conditions of electrolysis with controlled potential (analogous to classical polarography) it is sometimes possible to obtain a product of maximum purity, but from the economic viewpoint this type of synthesis is not suitable for industrial use. Moreover, the range of substances which may be reduced at controlled potential is much smaller than the range of compounds which react at controlled current. Oscillographic polarography with a.c. can be used to study phenomena occurring under conditions of preparative electrolytic synthesis in order to select the optimum conditions for this process. Thus Kalvoda[82] used oscillographic polarography to find the conditions under which the formation of organomercury compounds by the reduction of ketones at a mercury cathode takes place in highest yield.

One group of substances for which it has been possible, by means of oscillographic polarography, to follow electrochemical reactions and to compare these with the results of electrolysis at controlled current, consists of the aromatic carbonyl compounds[84,85]. It is found that under conditions of oscillographic polarography the reduc-

tion product of acetophenone, the pinacol, undergoes rearrangement in acidic solutions with the formation of the pinacone. This pinacone rearrangement can be readily followed oscillographically from the appearance of a new incision on the $dE/dt = f(E)$ curve during conversion of the pinacol, if 8 M sulphuric acid is used as support.

Study of the benzil–benzoin–hydrobenzoin–deoxybenzoin system shows that under conditions of oscillographic polarography the following series of reactions can occur:



Benzil on reduction gives an enediol, which is apparently oxidised, being revealed on the oscillogram by a corresponding anodic incision. No appreciable rearrangement of this enediol to benzoin is observed under the conditions studied. The product of the reduction of benzoin is slowly converted as a result of dehydration into deoxybenzoin in acid solutions. Under conditions of oscillographic polarography, however, the formation of deoxybenzoin during the reduction of benzoin may also take place *via* an intermediate radical as shown in the scheme. A characteristic feature of the reduction of benzaldehyde in 1 M H_2SO_4 is the formation of hydrobenzoin; in 8 M H_2SO_4, moreover, dibenzylmercury is formed during its reduction. The above scheme of reactions has been confirmed by an oscillographic study of various synthesised intermediate reduction products and comparison of all the data obtained by the different methods used in the interpretation of the oscillographic polarograms.

It may therefore be concluded that oscillographic polarography with a.c. can be used for the extremely detailed study of electrochemical processes in which organic substances take part. To obtain successful and convincing results, however, certain rules and working conditions must be observed. In the first place, it is necessary to use buffer solutions with different pH values as in ordinary polarography. It is also important to study the influence of the concentration of substance on the oscillopolarographic characteristics. Sometimes the nature of an incision can be determined from its shape, which changes during growth of the drop; in some cases the appearance or disappearance of new peaks or incisions is observed during growth of the drop. These phenomena may be due to the fact that during the increase in the drop surface, the current density at the surface changes. It is thus also necessary to study the influence of current density on the shape of the oscillographic curve.

3. Study of the Structure of Organic Compounds and Their Chemical Reactions

It was pointed out above that the adsorption of organic substances, particularly alcohols, is related to their molecular structure[54-56], so that the latter can be studied by oscillographic polarography.

The ease with which a depolariser accepts or donates electrons during an electrode reaction, and also the tendency for various artefacts to be formed, depend on the chemical structure of the polarographically active compound. Thus by using oscillographic polarography to study the mechanism of an electrode process in which an organic substance takes part, it is possible to reach certain conclusions regarding the reactivity of the compound.

In most cases, compounds which are related structurally are reduced polarographically at similar potentials, so that the compounds cannot be distinguished. Sometimes it is possible to distinguish isomers by classical polarography by making use either of the difference in the influence of substituents or of the difference in the influence of pH on the half-wave potentials of the isomers. In the latter case it is usual to find the pH range in which the difference in the half-wave potentials of the two isomers is a maximum. Since oscillographic polarography has a much higher resolving power than ordinary polarography, the former can be used in a number of cases to distinguish isomers with similar structures. Thus the oscillographic study of a mixture of isomeric nitrophenols was for a long time quoted as an example of the use of oscillography for this purpose[86].

In the study of the oscillopolarographic behaviour of any substance, it is important not only to obtain the oscillographic characteristics of this substance (the number of peaks or incisions on the curve, their potentials, etc.) but also to reach definite conclusions regarding the mechanism of the electrochemical process, which can be studied by the methods examined in the previous Section, and hence conclusions regarding the chemical structure of the compound.

Most papers on the oscillographic polarography of organic compounds published up to 1960 are purely descriptive. They generally give the oscillographic curves for the substances studied in solutions at different pH values and describe the incisions or peaks on the curves; the potentials of these peaks or incisions were not always measured. Although in these papers the polarographic results are often compared with the oscillographic data, the authors seldom reach conclusions regarding the mechanism of the electrode processes and the structure of the organic compounds.

Thus studies have been made of the polarographic and oscillographic behaviour of a number of 1-nitroalkanes[87] at different pH values, various esters of phthalic acid[88], and also tropone and tropolone[89].

The presence of two similar incisions on the cathodic and anodic branches of the $dE/dt = f(E)$ curve for an alkaline solution of benzaldehyde at similar potentials was taken as proof of the reversible reduction of this aldehyde at a dropping mercury electrode[90].

Pleticha[91] made a detailed study of the oscillopolarographic behaviour of butane-2,3-dione over a wide pH range and found that the depth of the corresponding cathodic incision on the $dE/dt = f(E)$ curve decreased in the same way as the height of the polarographic wave for biacetyl at a pH > 7.0. At pH ~ 9.0, biacetyl was detected oscillographically only at a concentration of 0.23 M. The depth of the cathodic incision for biacetyl increases with rise in temperature; this agrees with polarographic data, from which it was concluded that biacetyl molecules are hydrated in aqueous solution. The oscillograms for biacetyl show an anodic incision in addition to the cathodic incision. Since the assumed products of the polarographic reduction of biacetyl, *i.e.* acetoin and the pinacol of biacetyl, are,

according to the author's data, oscillographically inactive, the formation of these reduction products under oscillographic conditions cannot be responsible for the appearance of the anodic incision. Pleticha suggested that the anodic activity of biacetyl may be due to the formation of an unstable diol on reduction:

$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3 + 2e + 2H^+ \longrightarrow CH_3-\underset{\underset{OH}{|}}{C}=\underset{\underset{OH}{|}}{C}-CH_3 .$$

In Pleticha's opinion, this but-2-ene-2,3-diol is revealed anodically before it can be converted into acetone.

Aliphatic ketones containing a carbon–hydrogen bond next to the carbonyl group give only capacitive incisions on the $dE/dt = f(E)$ curves in alkaline solutions, but aromatic carbonyl compounds, in addition, show incisions due to electrolytic reduction[92] so long as the concentration of these substances does not exceed 10^{-4} M. With increase in their concentration in alkaline solution to 0.1 M, however, the oscillographic polarograms show additional cathodic incisions at a potential of about 0 V. These incisions are found on the oscillographic polarograms when the dropping mercury cathode, during charging, acquires the potential of the anodic dissolution of mercury. Incisions at about 0 V are not observed when a platinum cathode is used instead of mercury. Heyrovský[92] has recently shown that these incisions correspond to the formation of organomercury compounds by reaction of the enolic forms of the ketones in alkaline solution with bivalent mercury ions at a potential close to the extreme left-hand point on the $dE/dt = f(E)$ curve.

This reaction is not a sensitive test, since the concentration of enol in alkaline solutions is low; its detection by oscillographic polarography can be used successfully, however, to prove the presence of the $O=\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-H$ group in a molecule.

Urea, urethane, and certain other related compounds give analogous incisions on the $dE/dt = f(E)$ curves at a potential of about 0 V.[92] Dušinsky[93], however, considers that these are capacitive incisions.

The higher aliphatic acids and their esters are polarographically inactive. The oscillographic $dE/dt = f(E)$ curves for these compounds, however, give characteristic incisions[8,34]. The shape of the incisions for alkaline solutions of aliphatic acids is independent of the structure of the acid molecule. Their depth at a given molar concentration of acid, however, depends on the structure, and decreases, for example, with increase in chain length in the sequence $C_{13}H_{27}COOH$ (myristic acid), $C_{15}H_{31}COOH$ (palmitic acid), and $C_{17}H_{35}COOH$ (stearic acid).

It is found that, with aliphatic acids whose molecules contain the same number of carbon atoms, the depth of the oscillographic capacitive incision increases with increase in the number of double bonds in the acid molecule.

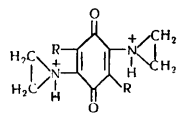
Oscillographic polarography with a.c. has been used by Nygard[94] to study the reversibility of the electrolytic reduction of selenocystine, selenocysteine, and various selenium-containing acids of the type $HOOC(CH_2)_nSeSe(CH_2)_nCOOH$, where n varies from 1 to 4. By comparing their oscillopolarographic behaviour in the pH range 1–12 with that of the corresponding sulphur analogues, he found that rupture of the Se–Se bond takes place more readily than rupture of the disulphide bond during reduction at a dropping mercury electrode. In cyclic disulphides, however, such as 1,2-dithiolancarboxylic acids, in which the five-membered ring is in a state of strain, rupture of the disulphide group takes place about as readily as in the case of aliphatic diselenidodicarboxylic acids.

Unlike trialkyl phosphates whose solutions give only distinct capacitive incisions on the $dE/dt = f(E)$ curves, trialkyl phosphites, at positive potentials on the electrode surface, apparently produce an artefact which forms an intermediate compound with mercury and undergoes the Arbuzov rearrangement[95].

Recently, Damokos[96] made an oscillopolarographic study of alkoxysilanes of the type $Si(OR)_4$ and $SiR'_n(OR)_{4-n}$, where $R = C_2H_5$, C_3H_7, and C_4H_9, and $R' = C_6H_5$ and CH_3. It was found that the oscillopolarographic activity of ethoxysilanes is greater than that of propoxy- and butoxy-silanes, and is proportional to the number of ethoxy-groups in the molecule of the orthosilicic acid derivative. Damokos also compared the adsorption activity of alkoxysilanes with structural factors such as the dipole moment of the molecule (see Table 3).

By using oscillographic polarography with a.c. the Vogel–Kemula hanging mercury drop method, a.c. polarography, and the oscillographic $i-E$ method to study the reversibility of the reduction of certain azo dyes, Horn[97] found that aminoazo-compounds, for which a quinoid structure is possible, are reduced reversibly from alkaline solutions, whereas hydroxyazo-compounds, which cannot form a quinoid structure in alkalis, are reduced irreversibly.

Benzoquinones containing two ethyleneimine rings, of the type



are also reduced reversibly[98]. Using a jet electrode and a special method for the rapid recording of oscillopolarograms, Berg[98] followed the mechanism of the successive splitting of the ethyleneimine rings during their reduction and acid hydrolysis initiated by ultraviolet irradiation.

Of the various heterocyclic compounds, the derivatives of pyridine have been studied in most detail. Volke's work showed that pyridinecarboxylic acids[99] and some of their derivatives[100] exhibiting similar polarographic behaviour are readily distinguished by oscillographic methods.

TABLE 3.

Compound	Depth of incision at 0.006 M, relative units	Dipole moment μ
Ethoxytrimethylsilane	16.5	1.146
Diethoxydimethylsilane	32.0	1.358
Triethoxymethylsilane	48.0	1.678
Ethoxytriphenylsilane	15.5	1.250
Diethoxydiphenylsilane	28.0	—
Triethoxyphenylsilane	43.0	1.538

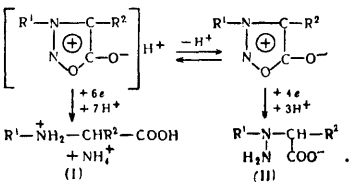
Nicotinamide and the hydrazide of isonicotinic acid are probably reduced by the same mechanism, which differs from that of the reduction of the acids themselves. The anodic incision on the oscillogram for an alkaline solution of the hydrazide of isonicotinic acid is apparently due to reaction between the hydrazino-group of the hydrazide and mercury ions at the dropping mercury electrode, analogous to the reaction of free hydrazine, with formation of a sparingly soluble substance.

The nitriles of all three isomeric pyridinecarboxylic acids are reduced comparatively readily at a dropping mercury electrode [101]. Volke [102] found that with most pyridine derivatives there is a difference in the course of the reduction between the 2- and 4-isomers on the one hand and the 3-isomers on the other. In the case of the cyanopyridines [101], however, there is a considerable difference between the polarographic and oscillographic behaviour of 2-cyanopyridine and that of 4-cyanopyridine. Study of the oscillopolarographic behaviour of the three isomeric pyridinealdehyde oximes [103] showed that the primary electrochemical process is reduction of the azomethine group with formation of the corresponding amine. In weakly acidic acetate solutions under oscillographic conditions, the amines formed may undergo electrochemical deamination at the electrode surface, revealed by an additional cathodic incision on the $dE/dt = f(E)$ curves for the oximes. The aminomethyl group probably reacts at the electrode in the protonated form. Volke confirmed the results of the oscillographic study of the pyridinealdehyde oximes by preparative electrolysis at constant potential.

In a study of the "2,2'-pyridoin–2,2'-pyridil" redox system, Holubek and Volke found that the former compound may not only undergo polarographic reduction but also polarographic oxidation to the di-2-pyridyl diketone. Reduction of the latter, however, yields 2,2'-pyridoin; this was followed oscillopolarographically [104].

Other heterocyclic derivatives of pharmacological importance which have been studied by the oscillographic method include acridines [105], phthalazines, and some pyrimidines [106].

In a study of the course of the polarographic reduction of sydnones in the pH range 0–12, Zuman [107,108] used oscillographic polarography to confirm certain stages in the electrochemical process. Sydnones in acidic solutions are reduced in the protonated form, whereas the non-protonated form is reduced at higher pH values; the half-wave potential of sydnones in weakly alkaline solutions is independent of pH.



The presence of ammonium ions in the reaction mixture after the reduction of sydnones in acidic solutions proves that process (I) occurs. Scheme (II) is confirmed by data obtained in the oscillographic study of sydnones in weakly alkaline solutions. The presence of positive incisions and peaks on the anodic branches of the $dE/dt = f(E)$ and $i = f(E)$ curves in the potential range in which the hydrazino-group reacts at a dropping mercury electrode indicates that the products of the reduction of sydnones at pH > 8 contain a hydrazino-group in the molecule. The fact that the half-wave potential of the sydnones is independent of pH in alkaline solutions enabled Zuman to assume that the potential-determining stage in the reduction of sydnones involves the addition of one electron to the sydnone molecule, and that the attachment of subsequent electrons and protons has no influence on the initial electrochemical act. This hypothesis agrees with the shape of the $dE/dt = f(E)$ curves for the sydnones in weakly alkaline solutions; these curves show several incisions. The formation of a hydrazine derivative according to scheme (II) was established by Zuman by means of polarography with a Kalousek switch and by electrolysis at a controlled potential.

The thiazoles are another group of heterocyclic compounds which have been studied by the oscillographic $i-E$ method [109].

The use of oscillographic polarography to study the chemical properties and reactions of physiologically active compounds and natural products with complex structures is extremely attractive and promising. The analytical oscillographic determination of alkaloids and amino-acids which are polarographically inactive has been mentioned above.

The oscillograms for most alkaloids show characteristic capacitive incisions or peaks, which are most clearly developed in alkaline solutions. In a number of papers on the oscillographic polarography of alkaloids, it has been pointed out that the storage of alkaloid solutions is accompanied by changes which can be followed oscillographically from the decrease in the depth of the incision [8] until, in some cases, the latter disappears completely. This behaviour is shown, for example, by ester alkaloids of the tropane group (Fig. 9).

Dušinsky [110] found that the decrease in the depth of the capacitive incisions for alkaloids during storage of their alkaline solutions is due to hydrolysis, and he used oscillographic polarography to study the kinetics of hydrolysis; it was found that oscillography was in this case superior to all other methods previously used for these purposes.

Dušinsky studied the hydrolysis of atropine (the tropine ester of tropic acid), homatropine (the synthetic tropine ester of mandelic acid), scopolamine (the scopine ester of tropic acid), and cocaine (the methylecgonine ester of benzoic acid) over the concentration range in which the depth of the incisions for the alkaloids varies linearly with concentration. It was found that the hydrolysis products of the alkaloids in this concentration range were oscillographically inactive and did not interfere with study of the hydrolysis. Dušinsky determined the constants and activation energies (Table 4) for the alkaline hydrolysis reactions, using the usual methods of calculation.



Fig. 9. Oscillographic $dE/dt = f(E)$ curves [43] for 6.8×10^{-4} M atropine in 5.5 M NaOH at different lengths of time from addition of the atropine to the solution (s):
1) 50; 2) 75; 3) 130.

TABLE 4.

Alkaloid	$k_{OH^-}(20^\circ)$ litre mole^{-1} s^{-1}	Activation energy, kcal mole^{-1}
Atropine	$5.1 \cdot 10^{-3}$	13.4
Homatropine	$2.7 \cdot 10^{-2}$	12.1
Scopolamine	$1.7 \cdot 10^{-2}$	11.5
Cocaine	$3.7 \cdot 10^{-2}$	11.6

The results obtained by Dušinsky agree with published data on the hydrolysis of these compounds. For example, the fact that the rate of alkaline hydrolysis of homatropine is six times that for atropine is attributed to the inductive effect of the electronegative hydroxy-group of mandelic acid [111].

In lithium hydroxide solution the polarographically inactive narcotine gives a cathodic incision on the oscillographic $dE/dt = f(E)$ curve. The depth of this incision gradually decreases, and a new cathodic incision appears at more positive potentials [112]. This change on the oscillogram for narcotine is due to cleavage of its lactone ring in alkaline solution with formation of a salt of narcotinic acid. Synthesised narcotinic acid in alkaline solutions gives oscillograms with the same incisions as those given by narcotine after cleavage. Similar phenomena were also observed with hydrastine. Changes in the shape of the oscillographic curve with time were established for physostigmine [105], apomorphine [113], and the veratrine alkaloids [47].

Molnar and Molnarova [48] made a detailed study of alkaloids of the quinine group — quinine, quinidine, cinchonine, cinchonidine, euquinine, aristoquinine, hydroquinine, optochine, eucupine, vusine, quinotoxine, and cinchotoxine — in various electrolytes. They found that the vinyl side-group of the quinuclidine ring has no influence on the oscillographic activity and behaviour of the alkaloids studied. The potential of the depolarisation incision of the alkaloid is influenced, however, by the nature of the substituent on the sixth carbon atom of the quinoline nucleus, and this is most marked in alkaline solutions.

The oscillopolarographic behaviour of the alkaloids emetine, *O*-methylpsychotrine, and emetamine, which are derivatives of isoquinoline, has been studied [114]. The oscillopolarographic properties of these alkaloids resemble those of 1,2,3,4-tetrahydropapaverine, 3,4-dihydropapaverine, and papaverine respectively.

Oscillographic polarography has been used to study another group of physiologically active compounds, related to the steroids and hormones. Thus Molnar [115] studied the oscillopolarographic behaviour of some 3- and 17-ketosteroids and their betainylhydrazones. The shape of the oscillographic curve for steroids in acidic aqueous–alcoholic solutions depended on the substituents attached to the steroid framework [116,117].

Of the vitamins, those of the B group have been studied in most detail by oscillographic polarography [118,119]. Pleticha [118] found that in alkaline solutions thiamine shows polarographic and oscillographic behaviour characteristic of compounds containing –S–, –SH, and –S–S– groups in the molecules. By comparing the behaviour of thiamine and cysteine, Pleticha explained the nature of the incisions on the oscillograms for thiamine.

Recently, oscillographic polarography has been used successfully to study the structure of nucleic acids. Paleček [120] found for the first time that nucleotides, nucleosides, and nucleic acid bases are oscillopolarographically active substances, and he used oscillography to study deoxyribonucleic acid (DNA) [121]. In ammonium formate solutions, DNA gives anodic incisions on the $dE/dt = f(E)$ curves at the same potential as deoxyguanylic acid. On this basis, Paleček suggested that the DNA molecule contains deoxyguanylic acid. To prove this he removed adenine and guanine from the DNA molecule by boiling in dilute hydrochloric acid, and studied the resulting apurinic acid by oscillographic polarography in the same ammonium formate solution. He found the apurinic acid to be oscillopolarographically inactive. Paleček also showed that the non-denatured DNA molecule contains deoxycytidylic acid, which, however, is revealed oscillographically only after denaturation of the DNA by boiling in dilute hydrochloric acid. Data obtained in the oscillographic study of deoxyribonucleic acid enabled Paleček to reach conclusions regarding the arrangement of the purine rings of guanine and the pyrimidine rings of cytosine in the DNA molecule.

Paleček's papers [120-124] describe in detail the results of the oscillographic study of nucleic acids and their bases.

The proteins haemoglobin, albumin [125,126], γ-globulin, and fibrinogen [126] have been studied by oscillographic polarography. Mach [126] studied the influence of thermal denaturation of the protein on the position of the incisions on the $dE/at = f(E)$ curves, and also examined the denaturing action of formaldehyde and hydrogen peroxide.

The capacitive effects produced on the $dE/dt = f(E)$ curves by amino-acids and certain peptides, and also the presence of various oscillopolarographically active groups in their molecules, made it possible to study the relationship between the structure and physicohemical properties of these substances and their oscillopolarographic characteristics [127].

Oscillographic polarography can be used to study the kinetics of reactions such as acid and alkaline hydrolysis, whose rates are comparatively low. It has been found possible to use the oscillographic $i-E$ method to characterise qualitatively the slow changes taking place in solutions of developers left to stand in air, to select the optimum conditions for development [128], and also to establish which of the developer oxidation products reacts with the colour components to form dyes under the conditions of colour development [129].

Oscillographic polarography also makes it possible to follow very rapid reactions, whose time of half-reaction may vary from 3 s to 0.01 s. Examples include the coupling of diazotised sulphanilic acid with sulphonated pyrazolone [130] and also the reaction of pyruvic acid with ammonia and the hydrolysis of coumarin [131].

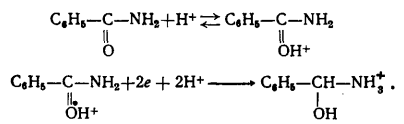
Oscillographic polarography makes it possible to calculate the kinetic rate constants for cases where the depolariser is formed as a result of a chemical reaction preceding the electron transfer stage. Thus Valenta [132] used oscillographic polarography with sawtooth voltage pulses to study the behaviour of formaldehyde in buffer solutions. He found that, at low rates of change of potential, the current is controlled by the rate of dehydration of formaldehyde. With increase in the rate of polarisation of the electrode, the influence of the kinetics of the hydration of formaldehyde diminishes, so that for the central pH range the current is determined by the concentration of free aldehyde present in equilibrium with the hydrated form. The equilibrium concentration of the non-hydrated form

and the dehydration constant of formaldehyde were calculated by comparing the height of the cathodic peak for formaldehyde with the height of the peak for the thallium ion under the same conditions. Volke and Valenta [133] made a similar study of the behaviour of the isomeric formylpyridines and determined their hydration constants from the oscillographic $i = f(E)$ curves.

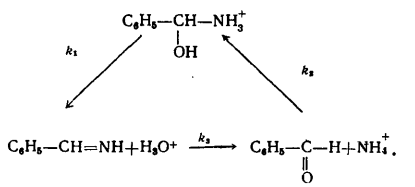
The application of oscillographic polarography to the study of such rapid reactions as the protonation of organic compounds would be extremely interesting, but no work has been carried out on these lines. Recently it has been shown that the "first" oscillopolarographic curves [134], and also, apparently, the hanging mercury drop method, can be used to study "surface" kinetic currents.

In the polarographic study of semicarbazones and thiosemicarbazones it was shown that, on passing from acid solutions to solutions of higher pH, there is an intensification of the kinetic restrictions associated with preliminary protonation of the molecules of the carbonyl derivatives [134]. These correlations, obtained from the results of a study of the semicarbazones and thiosemicarbazones based on current–time curves at the potential of the limiting current, were confirmed qualitatively by oscillographic polarography. The $dE/dt = f(E)$ curves for acidic solutions of these substances show sharp incisions whose shape corresponds to the diffusion character of their reduction. With increase in the pH of the solution, the depth of these incisions decreases, and they gradually approach the L-shaped form typical of a kinetic process. When 0.05% of gelatin is added to the solution, the incisions on the $dE/dt = f(E)$ curves for the semicarbazones and thiosemicarbazones almost disappear, again confirming their kinetic character [134,135].

Recently, Kalvoda and Budnikov [84,85] have shown that, under the conditions of oscillographic polarography, benzamide is reduced at negative potentials, whereas it is polarographically inactive. This reduction can be observed clearly by recording oscillograms with two dropping electrodes. The $dE/dt = f(E)$ curves for acidic solutions of pH < 2.5 show two kinetic incisions, which disappear when gelatin is added. During the reduction of benzamide in acidic solutions, the amino-alcohol is first formed:



This amino-alcohol is unstable in acid solutions and decomposes:



The benzylideneimine is also unstable in acid solutions, and decomposes to form benzaldehyde. The two incisions on the $dE/dt = f(E)$ curves correspond exactly to the reduction of benzaldehyde and its imine. With rise in the temperature of the solution and increase in the acid concentration, the incision for benzaldehyde becomes deeper, indicating an increase in the rate of decomposition of the imine and confirming the above reaction scheme. Behaviour analogous to that of benzamide is shown by nicotinamide, except that the oscillopolarogram for an acid solution of nicotinamide contains one incision corresponding to formylpyridine. The above scheme for the reduction of benzamide is applicable not only to oscillopolarographic conditions but also to the conditions of ordinary preparative electrolysis with controlled current, and is consistent with published data.

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The above factual material shows clearly the possible applications of oscillographic polarography in the study of organic compounds. Oscillographic polarography, however, is not a universal method of study, and it would be wrong to regard it as competing with classical polarography. The two methods rather supplement one another.

In order to use the advantages given by a combination of the two methods, it is necessary to known their possibilities for solving problems in organic chemistry. The possibilities of classical polarography have been discussed many times [136–139].

The above material shows that the advantages of oscillographic polarography are that it makes possible the study of phenomena which cannot be studied by ordinary polarographic methods, *e.g.* the formation of artefacts, and the analysis of a number of compounds which are considered inactive in classical polarography; it also makes it possible to obtain information much more rapidly.

Moreover, oscillographic polarography has much higher sensitivity and resolving power than the polarographic method. In classical polarography two waves can be observed separately if their potentials differ by not less than 200 mV, whereas in oscillography the difference in the potentials of the incisions or peaks which can be clearly distinguished should be about 100 mV, and in the case of the derivative curves ~ 40 mV. The method of oscillographic polarography with partial differentiation, developed by Nigmatullin and coworkers [140], has even greater resolving power and may in future play an important part in the study of organic compounds with similar structures.

There are other limitations at present on the use of oscillographic polarography for the solution of theoretical problems. In the first place, to obtain quantitative results it is necessary to take into account the state of the depolariser at the electrode surface, but this is not always possible because of the repeated a.c. polarisation. Even in the case of single-period oscillograms ("first curves") it is difficult to make allowance for this factor, since the form of the curve is influenced by the d.c. component, whose magnitude is often disregarded.

The theory of the oscillographic curves also takes into account several factors influencing the results obtained. Oscillographic polarography does not yet, however, exhibit the same definite correlations and simplicity characteristic of classical polarography. Neither fluctuations in current influencing the drop time of the mercury, nor periodic changes in the electrode surface leading to its vibration, complicate the overall picture of the electrode process in ordinary polarography.

The results obtained by the oscillographic method in most cases describe the electrode process to a first approximation, and at present there is, unfortunately, no case where oscillographic polarography has been used for the

quantitative study of the mechanism of electrochemical reactions. In the case of the $dE/dt = f(E)$ curves, the depth of the incision is not directly proportional to the concentration of depolariser. This undoubtedly complicates the quantitative application of the oscillographic dE/dt method. The mutual influence of different depolarisers, present together in solution, on the shape of the incisions on the oscillogram also makes quantitative calculations difficult. Finally, the accuracy and the reproducibility of the oscillographic curves are as yet inadequate for quantitative theoretical studies, whereas this cannot be said of classical polarography. At the present time, oscillographic polarography is in the state in which classical polarography found itself in the 1930's. The number of compounds which have been studied by this method is also still small.

Oscillographic polarography is now developing rapidly. Basic factual material obtained by the oscillographic method is being extended. The results of studies should, however, be treated and presented in a fashion appropriate to the present state of physical and chemical knowledge. It is quite insufficient to restrict the presentation to a description of the experimental data. Conditions now permit a direct approach to the study of electrochemical processes by oscillographic polarography. The task now facing oscillographic polarography is to study the nature and the reasons for the appearance of incisions or peaks on oscillograms, and by means of them to provide a fairly complete characterisation of the electrochemical process [8,140].

To permit comparison of results obtained by oscillographic and classical polarography, it is necessary to use polarisation at low frequencies (single-period curves). The interpretation of oscillographic curves is greatly facilitated by the use of a polarographic method in which an a.c. voltage of constant and fairly low amplitude is applied together with a d.c. polarising voltage. In a number of cases good agreement has been observed between results obtained by this method and by the dE/dt method for surface-active compounds (various alcohols, narcotine, atropine, tryptophan, etc.). To interpret the oscillograms, it is also necessary to use ordinary polarography with a Kalousek switch, and polarography at a stationary mercury electrode. The use of oscillographic polarography to prove the formation of intermediate products in the electrochemical synthesis of organic compounds is also extremely promising. Recently, oscillographic polarography has been used successfully to study complex biochemical materials (amino-acids, steroids, alkaloids, etc.). Attempts to produce an atlas of oscillograms for the identification of organic compounds are of interest in this connection, since in some cases even the shape of the curve may be of assistance in analysis.

The present review has not dealt with the possibilities of each method of oscillographic polarography, and it has not examined the advantages of methods involving the use of sinusoidal and sawtoothed or triangular voltages applied to the polarographic cell. It has also neglected problems associated with the use of methods in which $i = f(t)$, $E = f(t)$, and $dE/dt = f(E)$ curves are studied.

A combination of these methods will undoubtedly extend considerably our ideas regarding the nature of electrochemical processes involving organic compounds.

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Arbuzov Chemical Institute,
USSR Academy of Sciences