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Present State of the Oscillopolarographic Method of Analysis

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This review considers the main achievements of oscillographic polarography with a given form of polarisation voltage. Methods for increasing the sensitivity and resolving power of this analytical method and its use as a method for studying the mechanism of electrochemical processes are discussed. The influence of various factors determined by the composition of the solution in the cell and by the nature of the substances being studied on the form of the oscillopolarographic curves, and the characteristic features of the use of the method in the analysis of inorganic and organic compounds are examined. The bibliography contains 238 references.

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I. INTRODUCTION

Recent years have been characterised by further development of the oscillopolarographic method of analysis. A number of new papers have been published, in which considerable attention has been paid to the theory of the method and to its various practical applications; papers demonstrating the advantages of oscillopolarography as a highly sensitive method of analysis over other electrochemical methods have been published. Oscillographic polarography is at present used in organic, bio-organic[1], analytical, and physical chemistry, pharmacology and medicine, clinical studies and therapy, geochemistry, oceanography, and botany. Thus the materials studied include not only synthetic laboratory mixtures, but also natural materials such as minerals, petroleum, living tissue, plant materials, etc.

Recently, however, the accepted description of the method as "oscillographic polarography" has often been replaced in non-Soviet literature by other descriptions; this introduces certain difficulties, and sometimes even confusion. To standardise terminology and facilitate the classification of electrochemical (particularly polarographic) methods, and to permit generalisation of the results of studies by different workers using essentially the same method under different descriptions, the term "oscillographic polarography" should be preserved, although it may be noted that this description does not fully reflect the essential features of the method. In this method, in which the rapid change in the electrode potential brings about a rapid change in current strength, the polarisation curves are recorded with an inertia-free instrument—a cathode-ray oscillograph; hence the name of the method. The oscillograph, however, is also used, together with a string galvanometer, to record the current–time curves at constant potential, and also to record curves in chronopotentiometry[2] and other relaxation electrochemical methods[3] used to study the kinetics and mechanism of electrode processes. On the other hand, in oscillographic polarographs the rate of increase in potential can be varied within certain limits, and it can be made relatively small, comparable with the rate in classical polarography. Thus there is no sharp distinction between these methods[1,4].

The present state of oscillographic polarography is characterised by considerable variety in the versions of the method and the associated techniques of oscillopolarographic measurement[5-9]. These versions are classified according to four familiar features[6], of which the chief is the form of the polarising voltage. The latter determines to a considerable extent the electrical circuit and the oscillopolarographic assembly. Depending on the form of polarising voltage, it is possible to distinguish methods involving a linear polarising pulse—saw-tooth, symmetrical triangular, etc.—and methods involving a potential which changes non-linearly, for example according to a sinusoidal law.

The method involving the recording of the plot of $I = f(E)$ with a linearly changing voltage is called Randles–Sevcik oscillographic polarography; other names encountered in the literature are: voltammetry with continuously changing potential, voltammetry with change in potential or with scanning of the potential, and chrono-amperometry with scanning of the potential (particularly in the American literature[9]). Another method of oscillographic polarography—with a given sinusoidal current[7]—makes it possible to obtain oscillopolarograms in the form of the plots of dE/dt against E (these curves give the dependence of the rate of change of potential at the polarised electrode on its potential).

The method involving the recording of the $dE/dt = f(E)$ curves has been developed chiefly by the Prague school of polarographers. Regular symposia on oscillopolarography, and special courses for the training of specialists have helped the development and extensive application of this method of analysis in Europe[10-12], and papers have recently been published by South American workers[13]. The method involving the recording of $I = f(E)$ curves has also developed considerably in recent years, and there has been a marked increase in the volume of factual material obtained by this method.

In the Soviet Union this has been assisted by the mass production of the Soviet OP-1-61 oscillopolarograph and more particularly the PO-5122 01-02 and 02A oscillopolarographs.

The fact that recent work has not been reviewed makes it somewhat difficult to evaluate the main achievements of oscillographic polarography. In the present

review an attempt is made to fill this gap and to give a picture of the present state of this physicochemical method of analysis.

Most attention has been paid to the method involving the recording of $I = f(E)$ curves, since the other method mentioned above has been dealt with fairly fully in an earlier review[1]. Where necessary for comparison, however, data from papers dealing with the method involving the recording of $dE/dt = f(E)$ curves are introduced.

II. SOME THEORETICAL ASPECTS OF THE STATE OF THE OSCILLOPOLAROGRAPHIC METHOD OF ANALYSIS

1. Sensitivity and Resolving Power, and Methods for Increasing Them

The analytical applicability of classical and oscillographic polarography is usually estimated on the basis of the sensitivity and resolving power of the method. The sensitivity is characterised by the magnitude of the minimum concentration which can be reliably determined from the oscillopolarogram, and the resolving power is determined by the possibility of carrying out the simultaneous polarographic study of two substances. Resolving power with respect to potentials and resolving power with respect to concentrations are distinguished. If a single polarographic cell is used for the polarographic study, that is if the difference method, discussed below, is not used, and if the method involving build-up at the electrode is not used, the minimal concentration of a substance, undergoing reversible reduction, which can be determined in the solution is 5×10^{-7} M [4], with a resolving power with respect to potentials equal to ~40 mV [14] (for a polarising voltage of linear form).

The chief factor limiting the sensitivity of modern oscillographic polarographs is the capacity current. The total current for electrolytic reduction, recorded by the oscillograph, consists of the Faraday current I_e of the electrochemical reaction, associated with the transfer of electrons, and the capacity current I_c, which appears as a consequence of the existence of the electrical double layer. The sensitivity of the oscillopolarographic method is determined not by the magnitude of the total current but by the ratio of the "useful" current I_e to the current I_c, which represents an interference in analytical determinations. The rate of change in the polarisation potential V at low concentrations of the substance being studied can be decreased, in order to increase the ratio I_e/I_c, only to a certain limit. At low values of V, even without this, the small value of I_e decreases to such an extent that it becomes commensurate with background in the apparatus, and at high values of V the value of I_e is lost against a background which is many times greater than I_c. Thus decrease in the capacity current without change in I_e would mean an increase in the sensitivity of the method. For this reason, the developers of new apparatus have sought new methods of eliminating or decreasing the interference from I_c. For a long time, however, the solution to this problem in oscillopolarography was unsatisfactory. For example, in the slightly more sensitive electrochemical method of alternating-current polarography, the capacity current is eliminated by a variety of methods which make use of a special form of polarising voltage and special apparatus[3], whereas in oscillographic polarography, until recently the capacity current was eliminated only by linear compensation, which is insufficiently effective, however, since the capacity of the double layer shows a non-linear dependence on potential.

The earliest oscillographic polarographs had a comparatively low sensitivity, and the values of the parameters mentioned above were not achieved immediately. Comparatively recently, the difference method of oscillographic polarography has made possible the reliable determination of cadmium, lead, and zinc ions at concentrations down to 10^{-6} M, so that ordinary (not difference) oscillopolarography had an even lower sensitivity.

Subsequent work improved the electronic systems and the design of the individual blocks of oscillographic polarographs[16-18], and developed a circuit for the partial compensation of the capacity current[17]. One method for eliminating the capacity component and other interfering components of the current passing through the cell was the method of difference oscillographic polarography, developed by Pozdeev[19]. This makes it possible to increase both the sensitivity and resolving power of the analysis[5,15], since it gives a significant increase in the ratio I_e/I_c by presenting an oscillographic curve from simultaneous electrolysis of solutions in two identical cells. For example, this method can be used to eliminate the undesirable components of the current, associated with contamination of the electrolyte, the presence of large concentrations of other substances, and charging of the capacity of the double layer.

This method has been used to solve other problems[4], but it has several disadvantages. In addition to the fact that its use requires two cells, with a consequent increase in the complexity of the apparatus, the efficiency of this method of polarographic study is limited by the error in the subtracting assembly, and also by the difficulty of selecting two identical dropping mercury electrodes[9]. Thus the sensitivity of the difference method[14] achieved at present is 1.5×10^{-7} M, which is much greater than that of modern oscillographic polarographs operating with one cell (5×10^{-7} M) [20,21].

The theoretical and practical development of an oscillopolarographic method with a much lower level of capacity current than existing methods was achieved by Vyaselev[22]. The method was based on the principle of time selection, which makes it possible to separate the capacity and Faraday currents. In accordance with this principle, when a sudden change in potential is applied to a polarographic cell, the capacity current is damped more rapidly than the Faraday current. The current of the electrochemical reactions proportional to $t^{-1/2}$, whereas the capacity current is proportional to $e^{-t/RC}$, where R is the ohmic resistance of the cell and C the capacity of the double layer. Thus after a certain time interval from the moment when the sudden change in potential is applied, the current passing through the cell will be determined chiefly by the Faraday component. The idea of the possibility of using a step-like form of polarising voltage in oscillographic polarography was first put forward by Barker[23,24]. For a long time before Vyaselev's work[22], however, the idea was not realised, either theoretically or in practice. The theoretical study of the dependence of the diffusion current on the step-like polarising voltage showed that for step-like voltage, the measured values of the capacity current are in fact much smaller than those for a linear voltage[25,26]. This led to the development of an oscillopolarographic method in which the polarising voltage is applied in the form of sudden exponential increases[27]. Theoretical problems of oscillographic polarography with stepwise change in the polarising voltage were solved by

Vyaselev and Nigmatullin [25,26] and by Lingane and Christie [28,29]. The sensitivity of the method with step-like voltage (with respect to cadmium chloride solution) is 5×10^{-8} M, which is greater by an order of magnitude than that of the method using a linearly-changing voltage [26].

In addition to the difference method [19], differentiation of the oscillopolarographic curve [6,14,16,17] has been used to increase the resolving power. The analytical expression for the first derivative of the curve $I = f(E)$ was determined by Shekun [30], who showed by calculation that the height of the peak on the first-order differential oscillopolarogram $dI/dE = f(E)$ is a linear function of the concentration of depolariser; this makes it possible to use the relationship for quantitative analysis, as in classical polarography.

Unlike the first derivative of the classical integral polarogram, the oscillographic differential polarogram shows a negative peak as a consequence of a decrease in the current on the original curve, and the potential of its maximum does not coincide with $E_{1/2}$. This form of oscillopolarogram with negative peak makes the interpretation difficult, particularly in the study of multicomponent systems, and it is not convenient for analytical purposes.

Nigmatullin [31] was the first to show that for a reversible electrode reaction, the oscillopolarographic relationship $I = f(E)$ is a fractional derivative, of half-order, of the classical integral polarisation curve. On this basis, it was suggested that not ordinary differentiation, but half-order differentiation, that is so-called fractional differentiation, of the oscillographic curve be used to improve the resolving power of the method. The fractionally-differentiated oscillopolarogram obtained in this way corresponds in appearance to the first derivative of the classical integral polarogram, that is it does not have a negative peak and can be used for analytical purposes.

By combining the methods of difference oscillopolarography [19] and differentiation of the oscillopolarograms [6], Davis and Rooney [14] were able to obtain the second derivative of the oscillopolarogram, which gives good qualitative resolution with respect to potentials, but which is inconvenient for quantitative treatment.

Because of the mutual influence of different depolarisers, present simultaneously in the solution, on the shape of the peaks on the oscillopolarograms, quantitative calculations do not always have sufficient accuracy and reproducibility. To increase the accuracy of the measurement, Gokhshtein and Gokhshtein [32] proposed a method for extending the descending branch of the oscillopolarogram when the wave of another component was superimposed on it. The method gives satisfactory results if there is no appreciable capacity current; it can therefore be used successfully only at comparatively high concentrations of the substances being studied, when the capacity current is satisfactorily compensated by a linear method.

In oscillographic polarography with a polarising voltage of linear form, the relationships for the height and position of the peak on the oscillopolarogram are derived with the condition that the potential of the micro-electrode is a linear function of time [33,34]. As a consequence of the decrease in voltage across the ohmic resistances of the electrolytic cell and the elements of its circuit, however, this relationship is not observed for the change in potential under the conditions of the experiment. As a result, the oscillographic wave is extended, its height decreases, and the peak is displaced towards more negative potentials and becomes less sharp, so that the sensitivity of the measurements decreases. With very high ohmic resistances, the wave is completely "flattened", and the study becomes impossible. These phenomena have been observed experimentally, and in particular have been reproduced in an electric model [35-38] and have been the subject of discussion [39]. A special assembly has been designed [40] to compensate the cell resistance and obtain an oscillographic curve suitable for treatment, and also to increase the accuracy of the measurements. It successfully combines automatic compensation of the volume resistance with manual control, proposed by Valenta and Vogel [41]. The automatic compensation of the volume resistance is achieved by the oscillographic polarograph together with a three-electrode cell of special design. The method used for the controlled compensation of the volume resistance involves in practice a gradual increase in the feedback signal until the polarogram on the oscillograph screen corresponds to the theoretical. This form of compensation is less convenient, since in each specific case it requires the selection of the feedback signal in relation to the magnitude of the cell resistance. This method can be used, however, to estimate the magnitude of the compensated resistance.

Oscillographic polarography has recently become one of the highly sensitive methods which can be used for the analysis of traces of elements [42]. Despite the fact that data on the accuracy, sensitivity, and resolving power of this method have been published, it cannot be considered that these problems have been sufficiently fully studied from the methodological viewpoint.

It may be assumed that the dependence of the error in the measurement on the concentration of the substance being determined is of the form typical of micro-determinations [43], when the error increases close to the limit of the determination, since at this level of concentrations, the useful signal and the signal of the background (or blank experiment) are of comparable magnitude. The reliable measurement of signals at the level of the limit of the determination of substances and the "noise" of the oscillographic apparatus are metrological problems, and constitute one of the most important topics in measuring technology [44]. If the methods known as amalgam polarography with build-up (APB) [45] and film polarography are used, the sensitivity can be increased; these methods are examined in considerable detail in the literature.

Another method for increasing the sensitivity of polarographic determinations is based on the adsorption of the molecules of the depolariser on the electrode surface. Many reactions at an electrode take place with the participation of adsorbed species [46]. The concentration of these species at the electrode surface may be many times greater than their concentration in the volume of the solution. Thus when the polarographic voltage is applied to the cell, the reduction current in the first moments of time should be much greater than the value which might have been reached in the absence of adsorption; this makes it possible in principle to alter considerably the magnitude of the concentration minimum being determined.

The possibility of the practical realisation of this experiment was first demonstrated by Kalvoda and the present author [47,48] for the example of various organic substances (benzophenone, dibenzylmercury, etc.) sparingly soluble in aqueous alcohol, and thiosemicarbazones [49].

For the effective utilisation of the phenomenon of adsorption to increase sensitivity, the following conditions are obviously necessary [50]: 1) for significant "enrichment" of the electrode surface in adsorbed molecules, sufficient time is required for the establishment of adsorption equi-

librium at the micro-electrode in dilute solution; in some instances about 1 h has been necessary[46]; 2) since the quantity of adsorbed molecules at the surface of the micro-electrode is comparatively small, the oscillopolarogram must be recorded in a short time interval, that is it is necessary to select a suitable rate of polarisation; 3) the oscillopolarograms should be recorded with improved apparatus which makes it possible to eliminate the charging current of the double layer capacity, for example an oscillographic polarograph with step-like voltage[26,27,50].

The use of the phenomenon of adsorption to increase sensitivity opens up extensive possibilities in the analysis of organic substances by oscillographic polarography. Although the method of APB can be used successfully to determine traces of ions in solution, this is impossible for organic compounds, for reasons which are well understood. For some classes of organic compound containing groups which are active with respect to the electrode material, such as aldehydes, ketones, derivatives of urea and thiourea, thiosemicarbazones, organic compounds of sulphur, etc., which react with mercury at positive potentials[1] with the formation of the corresponding organomercury compounds or mercury sulphide[51,52], however, it is possible to use the principles of film polarography. This involves essentially preliminary electrolysis of the solution being studied at the potential of the initial level of recording of the $I = f(E)$ curve, as a result of which the compounds mentioned above are formed on the electrode surface in the form of a film; with cathodic polarisation of the electrode they are revealed as sharp peaks corresponding to the reduction of the corresponding substances, and this is used for analytical purposes. For thiourea, the minimal concentration which can be determined by this method is 10^{-7} M [52].

The sensitivity of the oscillopolarographic method can also be increased by making use of the formation of sparingly soluble substances, with low degrees of dissociation, in the solution[53-56]. Decrease in the activity of a substance leads to a decrease in the extent to which it is adsorbed on an electrode surface[53]. Since for sparingly soluble substances the activity is inversely proportional to the change in solubility, decrease in solubility will lead to an increase in the degree of covering of the electrode surface, that is adsorption.

The mechanism leading to the increase in the depth of the peaks under the influence of anions is still insufficiently clear. It is probable that in addition to a change in the Ψ'-potential in solutions containing anions which are readily adsorbed on the electrode, some contribution is made by adsorption-chemical interaction of the anions with the atoms of the reduced metal. From this it follows that when the sensitivity of an oscillographic polarograph is established with respect to a given substance (cadmium salts are usually employed for this purpose), it is necessary to indicate the composition of the background. An increase in sensitivity is facilitated by the formation not only of sparingly soluble substances, but also of complexes of the ions being determined with organic ligands, with a low degree of dissociation[13,57,58]. Thus cobalt is readily determined in plant materials, from the oscillopolarograms of its inner-complex compounds with dimethylglyoxime[58].

An example of a process similar to this mechanism of concentration is apparently provided by the extraction of various ions of uranium, zirconium, mercury, and the rare earth elements from aqueous solutions by organophosphorus compounds present in the adsorbed state on the surface of a stationary electrode[59]. In this instance it is assumed that coordinate bonds are formed between the metal and the organophosphorus compound in the surface layer[60], leading to the accumulation of the substance and hence to an increase in sensitivity. This method of increasing sensitivity has essentially not yet been used in oscillographic polarography.

Finally, mention must be made of another way of increasing the sensitivity of the oscillopolarographic analysis of organic substances—the use of the salting-out effect. In early work on oscillographic polarography, concentrated base electrolytes (1 M or more) were generally used to decrease the resistance in the polarographic cell. For a number of organic compounds, increase in the concentration of the background is not without an effect, since the organic compound is usually salted-out from solution. The salting-out of organic substances from concentrated solutions of electrolytes leads to an increase in their surface concentration[61]. Thus if the last effect is observed, the heights of the peaks or teeth on the oscillopolarograms will increase with increased concentration of the background electrolyte, and this leads to an increase in sensitivity. Thus Kalvoda[62] showed for derivatives of benzoic acid that with increase in the KF concentration to 10 M, the determination of these compounds becomes possible, whereas in a background of the usual neutral buffer, almost no capacity effects are observed on the oscillopolarograms of solutions of these derivatives.

2. Form of Oscillopolarographic Curves and the Mechanism of Electrode Reactions

A source of information on the nature of an electrode process and the composition of a solution being analysed is provided by the oscillographic curve, the form of which depends on a number of factors.

Firstly, the form of the curve, and in particular the position of the peak with change in V depends on the type of electrode process and its characteristic features[1]. In earlier work[51,52,63,64], conclusions regarding the nature of the electrode reaction were generally reached on the basis of the rate coefficient, or the so-called "Semerano criterion"[1,65]. Recently, various diagnostic criteria have been derived for the investigation of the nature of the various stages of an electrochemical process, associated with the transfer of electrons and involving conjugated chemical reactions. For this purpose, Nicholson and Shain[66] proposed the use of not only the form of the change in current at the peak I_p with change in V, but also the dependence of such parameters as the potential E_p, the half-peak potential $E_{p/2}$ (when the peak is "flattened" over several millivolts along the axis of potentials), the width of the oscillopolarogram (the extent of the curve along the axis of potentials between the abscissae E_p and $E_{p/2}$), the ratio of the heights of the anodic and cathodic peaks I_{pa}/I_{pk} with change in V, and also the dependence of the current function Ψ (the current function Ψ is defined by the expression $I_p/nFAC_0\sqrt{Da}$, where I_p is the current at the peak, A the area of the electrode, C_0 the volume concentration of the depolariser, a a kinetic parameter $a = nFV/RT$, and the other symbols have their usual significance) on V. These criteria were derived for the usual conditions of oscillographic polarography with an electrode, the surface of which does not change during the recording of the curve. It should, however, be noted that the form of the oscillopolarogram for a definite form of polarising voltage depends on the type of electrode

used[4,67,68], that is on whether the electrode is liquid or solid, spherical, flat, or film, etc., on the dimensions of the space next to the electrode[69], on the ohmic factors of the cell[39,70], which depend on the concentration of the background electrolyte, and apparently on the nature of the solvent[4]. If the oscillopolarograms are obtained as the plots of I against E at a mercury electrode with a very short dropping period of ~0.008 s, the form of the curves is identical to that of the usual classical curves[67]. If the surface of the mercury electrode changes during the recording of the oscillopolarograms, the most suitable criterion for the calculation of I_p for different V and arrests of the polarisation pulse is the moment when the curve reaches E_p [71]. In principle the method of oscillographic polarography makes it possible to determine a number of parameters characterising the electrode process, such as a, the transfer coefficient; D, the coefficient for the diffusion of the substance towards the electrode; n, the number of electrons taking part in the electrode reaction; k_s, the reaction rate constant; and ΔG, the standard free energy of activation of the discharge process. Moreover, it is possible to establish the nature of the separate electrochemical stages, complicated by chemical reactions, the reaction rate constants, and the orders of the reactions, and to detect the formation of intermediate species during electrolytic reduction or oxidation. Usually, the relationships for the calculation of the parameters have been derived without allowance for the adsorption of depolariser species on the electrode surface, as for example in Ref. 66, or with the assumption that the contribution of adsorption is slight. For organic compounds this is only a particular case. The use of oscillographic polarography to study adsorption phenomena will be examined below.

If an electrode process is controlled by the rate of diffusion and the electron transfer stage is reversible or almost reversible and is not complicated by chemical reactions, the corresponding oscillopolarograms have a sharp maximum. E_p in this instance is independent of the depolariser concentration. The value of I_p is determined by the familiar equations of Sevcik or Randles[33,34,72,73], is independent of the pressure on the dropping mercury[74], and is directly proportional to $V^{1/2}$. For reversible processes, the following relationships are applicable[66,75]:

$$E_{p/2} - E_p = \frac{0.057}{n}(1) \quad \text{and} \quad E_p = E_{1/2} - (1.109 \pm 0.002)\frac{RT}{nF} \qquad (2)$$

or for an indistinct peak $E_{p/2} = E_{1/2} + 1.09\,RT/nF$, where $E_{1/2}$ is the polarographic half-wave potential, and R, T, and F are familiar constants. From the descending branch of the oscillopolarograms at potentials 0.2 V more negative than E_p, it is possible to determine n from the equation

$$I_p/I = n^{1/2} \cdot \text{const} \qquad (3)$$

derived theoretically[76] and later found empirically[77], and also the diffusion coefficient of the depolariser D[76]:

$$I_{0.2} = 1.43 \cdot 10^5 \cdot n \cdot A \cdot C_0 \cdot V^{1/2} \cdot D^{1/2} \qquad (4)$$

where $I_{0.2}$ is the current for a potential of $(E_p + 0.2)$ V. For reversible processes with diffusion control, moreover, the quantity $\Delta E_{p/2}/\Delta \lg V$ is independent of V [66]. If the electrode is polarised by a triangular voltage pulse, for a reversible process, an anodic peak is observed in addition to a cathodic peak, the ratio I_{pa}/I_{pk} is equal to unity[66], and ΔE_{pak} is $0.057/n$ V[78]. Study of the dependence of ΔE_{pak} on V makes it possible to find comparatively simply the value of k_s—the heterogeneous rate constant for the electrode reaction[78]. The chief source of error in this determination is the non-compensated quantity IR, which depends on C_0, V, and the concentration of the background in the cell. With increase in I, the ohmic potential drop will be commensurate with ΔE_{pak} so that it is necessary to take precautions to eliminate it or to make allowance for this effect in the calculations.

For an irreversible electrode reaction with diffusion control, I_p is determined by Delahay's equation[79]:

$$I_p = 2.99 \cdot 10^{-5} \cdot n \cdot A(\alpha n_a)^{1/2} \cdot C_0 \cdot D^{1/2}V^{1/2} \qquad (5)$$

where n_a is the number of electrons taking part in the potential-determining stage ($0 < n_a < 1$). The form of the curve for an irreversible process depends on αn_a, whereas the heterogeneous rate constant k_s defines only the position of this curve on the axis of potentials, that is it depends on E_p. Since $\alpha < 1$, and $n_a < n$, it follows that I_p for an irreversible process is less than I_p for a reversible process. To determine n it is possible to use Eqns. (3) and (4), which are also applicable for an irreversible reaction with allowance for the coefficient α. The transfer coefficient is found from Matsuda's relationships[75]:

$$\alpha = \frac{0.048}{n(E_{p/2} - E_p)} \qquad (6)$$

Comparison of the experimentally observed value of I_p for an irreversible process with that calculated theoretically from Randles' equation[73] also makes it possible to estimate α from the equation[75]

$$\alpha = \left(0.9\,\frac{I_p^{\text{exptl}}}{I_p^{\text{theor}}}\right)^2 \qquad (7)$$

On going to irreversible processes, for example with increase in V [76], the sharp form of the maximum on the oscillopolarogram is smoothed out, and the curve extends further along the potential axis than that for a reversible reaction, and the slope of its central section is given by the expression[66]:

$$E_p - E_{p/2} = -1{,}857 \cdot \left(\frac{RT}{\alpha n_a F}\right). \qquad (8)$$

The anodic peak for irreversible processes is absent, or else its potential is much greater than the theoretically permissible difference ΔE_{pak}. It has been shown that for an irreversible reaction the current passing in the initial section of the oscillopolarogram is independent of V [66,80]. E_p and $E_{p/2}$, however, are functions of V [66]:

$$(E_{p/2})'' - (E_{p/2})' = (E_p)'' - (E_p)' = \frac{RT}{\alpha n_a F} \ln \sqrt{\frac{V'}{V''}} \qquad (9)$$

that is with an irreversible process a cathodic shift of the peak or half-peak potentials by about $0.03/\alpha n_a$ is observed for each tenfold increase in the rate of polarisation. From the relationship for the current and potential of the electrode for irreversible reduction[66], as for Gokhshtein's equation[76], it follows that the plots of $\lg I_p$ against $(E_p - E_0)$, where E_0 is the formal electrode potential, for different V are given by straight lines with slope equal to αn_a, and with distance between them proportional to k_e°—the rate constant for direct electron transfer. This relationship is convenient for finding the kinetic parameters of an electrode reaction, although this requires

a change in V by several orders of magnitude. The value of k'_e can also be found from Matsuda's equation[75]:

$$\lg k'_e = 1.1339 - \lg f/\sqrt{D} + {}^1/_2 \lg(\alpha n_a) V + \frac{\alpha n_a E_p}{0.0591} \qquad (10)$$

where E_p is given relative to the potential of the hydrogen electrode, and f is the activity coefficient. This equation also shows that k'_e depends on E_p and V. The standard free energy of activation ΔG is given by the equation derived[81] from the equation of Delahay[79] and the Gokhshteins[32]:

$$\Delta G = F[\alpha n_a(E_a - E_p) - 0.0591 \lg I_p/nAC_0 + 0.54 + 0.0591 \lg 10^8 \cdot \rho] \qquad (11)$$

where E_a is the potential of the reference electrode, and ρ the distance to which the depolariser species approaches the electrode. Fig. 1 gives some of the graphs which

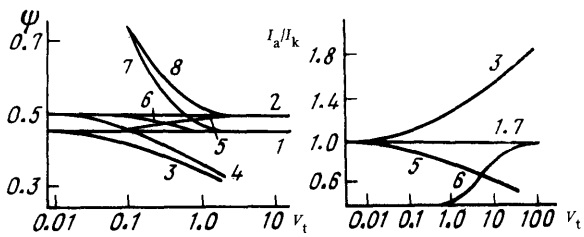


Figure 1. Dependence of the current function Ψ and the ratio I_a/I_k on the rate of polarisation[66]: *1*) reversible and *2*) irreversible charge transfer; *3*) reversible and *4*) irreversible charge transfer preceded by chemical reaction; *5*) reversible electron transfer, followed by a reversible chemical reaction; *6*) reversible charge transfer, followed by irreversible chemical reaction; *7*) catalytic reaction with reversible and *8*) irreversible electron transfer.

serve as diagnostic criteria for the main types of reaction mechanism[66]. It should be noted that Eqns. (5)–(11) are applicable with the condition that αn_a is independent of potential. Methods for finding the rate constants of the chemical reactions preceding, taking place in parallel with, or following the transfer of electrons have been examined by a number of authors[66,82-95]. Compared with classical polarography, oscillographic polarography makes it possible to extend the range for the determination of these quantities by four orders of magnitude. From the theory of kinetic currents in polarography it follows that for an electrode process taking place according to the scheme $L \underset{k_B}{\overset{k_f}{\rightleftharpoons}} O \overset{n_e}{\rightleftharpoons} B$, the upper limit is given by the expression $k_B = 200\ \tau^{-1}K^{-2}$ [46,82], where τ is the duration of electrolysis or the dropping period of the electrode, and $K = k_f/k_B$ the equilibrium constant for the chemical reaction. It follows from the last expression that in order to find the constants for very fast chemical reactions it is necessary to decrease the duration of electrolysis. In oscillopolarography, τ depends on the rate of polarisation. If it is assumed that $V = 500$ V s^{-1}, and that the polarisation pulse varies in the region of 1 V, then the duration of electrolysis is less than 2×10^{-3} s, and this makes it possible to study extremely fast chemical reactions taking place at the electrode. The practical restrictions here are that at such high values of V, there is a marked increase in I_c, as mentioned above. If the methods of difference oscillopolarography[19] or a stepped polarising voltage[26-28] are used, however, this restriction can be eliminated to a considerable extent. Essentially, for each chemical reaction preceding electron transfer, it is possible to find a range of V for which the $I = f(E)$ curves become independent of the rate of the chemical reaction. In this case the current recorded will be controlled by the diffusion of the substance O to the electrode and will correspond to a state of equilibrium between L and O. The value of K in this case is determined independently of the values for the rate constants of the chemical reaction. This method was used to determine the equilibrium constant for the hydration of formaldehyde[85] and the isomeric pyridine aldehydes[86].

The case where the reversible transfer of electrons is preceded by a chemical reaction of first order was examined by Saveant and Vianello[82]. Using the method of dimensionless parameters, they derived relationships characterising the dependence of the current function on the electrode potential for different values of K and k ($k = k_f + k_B$). The change in the parameter $\lambda = \frac{RT}{nF}\frac{k_f + k_B}{V} = \frac{kTk}{nFV}$ within certain limits makes it possible to change from pure diffusion current to currents controlled by a preceding chemical reaction. For $K > 20$ the current–potential curves have the usual form characteristic of diffusion-controlled processes. At smaller values of K the curves show kinetic limitation. For $K < 0.5$ the range of existence of kinetic currents is determined by the value of λ in the range

$$0.025 < \lambda < \frac{100}{K^2} \qquad (12)$$

For $\lambda < 0.025$ the rate of the chemical reaction is so low compared with V that during the polarisation pulse, significant formation of the substance O from L does not take place, and the current is controlled by the diffusion of O, the concentration of which is determined by the equilibrium $L \rightleftharpoons O$. For very low values of K the diffusion currents are very low and difficult to measure. However, since I_p is proportional to $V^{1/2}$, the measurement can be made at suitable values of V. For $\lambda > 100/K^2$ the rate of the chemical reaction is so great compared with V that the equilibrium at the electrode is established almost instantaneously, so that I_p is determined by the volume concentration of the depolariser. The $I = f(E)$ curves then show a cathodic displacement by an amount $\frac{RT}{nF}\ln\frac{K}{1+K}$ with increase in V by one order of magnitude. For intermediate values of λ, given by Eqn. (12), the currents are limited by the kinetics of the chemical reaction. If V changes in the range 0.1 – 500 V s^{-1}, the measured kinetic currents are determined by the range 0.1 s$^{-1} < k < 2 \times 10^6/K^2$ s^{-1} (for 25°). The form of the anodic peak on the oscillopolarograms obtained with a triangular voltage pulse is influenced by a preceding chemical reaction to a much smaller extent than the form of the cathodic peak[66]. In the work cited[66], a change in the quantities I_a/I_k, $\Delta E_{p/2}/\Delta \lg V$ and I_k with change in V was also detected, and it was recommended that these be used as diagnostic criteria. A particular case of reversible electron transfer with a preceding chemical reaction,

considered above, is a process of the type $L \underset{k_B}{\overset{k_f}{\rightleftharpoons}} 2\,O$; $O \overset{ne}{\rightleftharpoons} B$ [83]. For this the form of the oscillopolarogram depends on the value of a certain dimensionless parameter θ, proportional to the product $\frac{(k_B)^{1/2}}{V^{1/2}} \cdot K^{3/4} \cdot C_0^{-1/4}$ [83]. For very small values of θ the $I = f(E)$ curves have the form of integral polarograms, for which $E_{1/2}$ is given by the equation (for 25°):

$$E_{p/2} = E_{1/4} + \frac{0.041}{n} + \frac{0.03}{n}\lg n - \frac{0.03}{n}\lg k_B - \frac{0.015}{n}\lg K + \frac{0.03}{n}\lg V + \frac{0.015}{n}\lg C_0 \qquad (13)$$

For high values of θ the reduction current is diffusion controlled, and $E_{p/2}$ is not now dependent on V

$$E_{p/2} = E_0 + 0.01 + \frac{0.03}{n}\lg K - \frac{0.03}{n}\lg C_0 \qquad (14)$$

(with the condition that the diffusion coefficients of O and B have similar values) where E_0 is the normal redox potential of the O/B complex.

Irreversible transfer of an electron with a *preceding* chemical reaction of first order was examined in detail by Nicholson and Shain [66], who give the dependence of the calculated values of the current function on the parameters of the chemical reaction (K, $k_f + k_B$) for which equilibrium is established slowly, compared with discharge. Voloshin [84] used these calculations in a study of electrochemical processes with a preceding reversible chemical reaction of higher order $L + mz \rightleftharpoons B$ and found that a change in the concentration of z displaces the potential of the peak in the same way as $E_{1/2}$ changes with the pH of the solution for processes preceded by protonisation [46]. For this type of electrode reaction it is useful to study the dependence of I_p and $\Delta E_{p/2}/\Delta \lg V$ on V.

A paper already cited [66] discussed for the first time the case where the *rapid transfer* of electrons according to a reaction $L + ne \rightleftharpoons O$ is followed by a *reversible chemical* reaction $O \underset{k_B}{\overset{k_f}{\rightleftharpoons}} B$ (if the electron-transfer stage is retarded, the subsequent chemical reaction does not influence the form of the oscillopolarogram). A change in the value of the parameter $\xi = K\sqrt{\frac{nFV}{RT(k_f + k_B)}}$ by almost three orders of magnitude has little influence on the magnitude of the current function, so that to study the subsequent chemical reactions it is convenient to use the displacement of E_p with V. With change in the parameter ξ by one order of magnitude, E_p undergoes a cathodic displacement of almost $60/n$ mV, and tabulated data [66] can be used to estimate the parameters of the chemical reaction. The subsequent reversible chemical reaction has a marked influence on the anodic peak. It should, however, be noted that in this instance the depth of the anodic peak depends on the amplitude of the polarisation. Thus the dependence of the ratio I_a/I_k on ξ for the electrode reaction being considered must be obtained for some selected amplitude of polarisation.

If the *reversible transfer* of electrons is followed by an irreversible chemical reaction, taking place at a low rate, it has almost no influence on the form of the oscillopolarogram. For high values of the parameter RTk/nFV, however, the displacement of the potential of the cathodic peak with V can be used for a kinetic analysis [66]:

$$E_p = E_{1/4} - \frac{RT}{nF}\left(0.78 - \ln\sqrt{\frac{RTk_f}{nFV}}\right) \qquad (15)$$

It follows from Eqn. (15) that increase in the expression under the square root sign leads to an anodic displacement of E_p, whereas for the previous example a displacement of E_p towards cathodic potentials was noted. When the electrode is polarised by a triangular voltage pulse, useful information on the chemical reaction is obtained from the dependence of the quantity I_a/I_k on V, if allowance is made for the amplitude of the polarisation (or the time taken for E for the electrode to change from $E_{1/2}$ to the final polarisation potential) [66]. Saveant and Vianello [87] derived an expression for the dependence of E_p on C_0 for the depolariser and V for the case where the deactivation of the electrode products takes place as a result of their bimolecular interaction. From these equations it follows that the value of E_p should be displaced with increase in V, and $\frac{\Delta E_p}{\Delta \lg V} = \frac{RT}{nF}\left(\frac{1}{m+1}\right)$; with increase in C_0 the quantity E_p becomes more positive and $\frac{\Delta E_p}{\Delta \lg C_0} = \frac{m-1}{m+1}\cdot\frac{RT}{nF}$, where m is the order of the reaction with respect to the electrode products (for dimerisation, $m = 2$). The authors cited [87] point out that from the nature of the dependence of E_p on $\lg C_0$ it is possible to distinguish a process with retarded electron transfer from a process in which reversible electron transfer is followed by rapid dimerisation of the electrode products.

Electrode reactions with order greater than unity have been studied [88]. The $I = f(E)$ curves for polarisation of the electrode by triangular pulses were calculated by the published method [66] for processes $mO + ne \rightleftharpoons qL$ ($m > 1$), controlled by diffusion. It was found that for $m = 2$ and 3, the peaks are lower and broader than the peaks corresponding to a first-order reaction, examined above [66]. The theoretical calculations were verified experimentally for the example of the dissolution of mercury in potassium cyanide solutions ($m = 2$ or 3, depending on the cyanide concentration).

The catalytic reaction, in which the reversible transfer of electrons to the molecule of the depolariser O is accompanied by its parallel regeneration under the influence of the catalyst Z,

$$O + ne \rightleftarrows B, \quad B + Z \xrightarrow{k_f'} O$$

was discussed in detail by Saveant and Vianello [89], and later by Nicholson and Shain [66]. For a given value of k_f' and concentration of the catalyst, change in V gives a family of curves with a common asymptote, the ordinate of which is independent of V and is determined by the expression

$$I_{lim} = nFA\sqrt{C_Z D k_f'} \qquad (16)$$

Eqn. (16) can be used to find k_f'. The parameters of the catalytic reaction can be studied by means of triangular voltage pulses, for which the form of the oscillopolarograms depends on the magnitude of RTk_f'/nFV [66],

and also from the dependence of $\Delta E_p/\Delta \lg V$ on V. For a catalytic system of this type the ratio I_a/I_k is equal to unity and is independent of V, as in the case of reversible transfer of electrons, not complicated by chemical reactions[66].

For a system in which *the electrochemical and chemical stage* of catalysis are *irreversible*, the results obtained are analogous to the previous example, but the peaks in this instance will have a smaller height and will be slightly more extended along the axis of potentials. The form of the wave depends on the parameter $\frac{RTk'_f}{\alpha n_a FV}$. Saveant and Vianello[90] recommend for the determination of k'_f the measurement of the dependence of the ratio of the limiting catalytic current to the current for a given rate of polarisation on V.

An interesting type of electrode reaction is that corresponding to processes which take place by the so-called ECE mechanism, that is when there is a chemical reaction $L \overset{n_1 e}{\rightleftharpoons} O \overset{k_f}{\rightarrow} B \overset{n_2 e}{\rightleftharpoons} Z$ between the electrochemical stages. The oscillopolarograms may have different forms, depending on the relative ease of reduction of the depolariser species L and B, and also on the extent to which the chemical reaction and the electron transfer stage are reversible. In general, the study of its dependence on the parameters of the electrode reaction is very complex. Examples where the chemical stage is irreversible[92-94], and the transfer of electrons takes place rapidly[92-94] or is retarded[92], have been examined. If both transfers of n_1 and n_2 electrons are reversible, and the difference in the ease of reduction of the species L and B (that is their $\Delta E_{1/2}$ values), is sufficiently large and it is more difficult to reduce B than L, then the curves contain two peaks, the form of which is determined by the parameter RTk_f/nFV and the ratio n_2/n_1. At low values of this parameter the second peak is not observed, and with increase in the parameter the peak height increases. The form of the anodic peaks depends to a considerable extent on k_f and the extent of polarisation of the electrode, so that it is difficult to obtain information on the process from it. The calculated values of the current function for the reversible and irreversible transfer of electrons for different values of the kinetic parameter n_2/n_1 and $E_{1/2}$ [92] make it possible to determine k_f for the chemical reaction included. For example, a detailed study was made of the reduction of *p*-nitrosophenol, which takes place by an ECE mechanism[93]. The values obtained for k_f show good agreement with results obtained by other electrochemical methods. For cases analogous to *p*-nitrosophenol (for $n_1 = n_2$), it is convenient to determine k_f by means of the equation

$$I_k/I_d = \frac{0.4 + \frac{RTk_f}{nFV}}{0.396 + \frac{RTk_f}{nFV} \cdot 0.469} \qquad (17)$$

where I_k is the height of the kinetic peak, measured at a certain value of V, and I_d is the magnitude of the current, calculated with the assumption that there is no chemical reaction, or measured at high values of V.

Despite the extensive possibilities provided by oscillographic polarography for the study of the mechanism of electrode reactions, the number of papers in which the theory of the method has actually been used for this purpose is small. Thus the value of k_s for the reduction of the cadmium ion in 1 M KCl has been determined[78], and values of α, n, k_s, D, and the free energy of activation for reduction at a dropping mercury electrode (d.m.e.) have been found for the ions of europium[96], indium and antimony[97], and silver in alkali metal nitrate solutions[98], and of silver, cadmium, lead, copper, and indium in a eutectic mixture of sodium and potassium nitrates at 245° at a platinum electrode. In the last work cited, it was established in which of the systems the reduction product is oxidised to the oxide by nitrate, or the metal forms an alloy with the electrode material. The reversible discharge of a substance with constant activity, accompanied by irreversible combination of the reaction product at the electrode has been studied in detail for the example of the anodic dissolution of mercury in sodium sulphide solutions[100].

Study of the mechanism of the reduction of sulphur dioxide in acid media at a mercury electrode showed that under these conditions, hydrogen sulphide and elementary sulphur may be formed[101].

The method of oscillopolarography with triangular scanning of the voltage has been used to study the stability and ligand exchange of mixed porphyrin complexes of Fe^{III} with cyanide and pyridine in solution at a platinum electrode[102] and ligand exchange in the product of the reduction of Fe^{III} acetylacetonate in acetonitrile[103], and to study the kinetics of an electrode process involving ionic complexes of zinc with hydroxide ions and ammonia at a stationary mercury film electrode[104]. The method was used to study the kinetic parameters and the nature of the reduction of the nitriles of acrylic, vinylacrylic, and cinnamic acids[105] at a mercury electrode, Cupferron at a carbon paste electrode[106] and a d.m.e.[107] in aqueous alcohol, diphenylpicrylhydrazyl in tetrahydrofuran at a platinum electrode[108], and isomeric cyanopyridines[109]. Study of the dependence of E_p for the peak on V and C_0 for the tropylium cation showed that in its one-electron reduction at a d.m.e., dimerisation of the radicals takes place[110]. In the reduction of benzanthrone in acidic aqueous alcoholic solutions, however, in addition to the peak corresponding to the transfer of one electron with subsequent dimerisation of the product, at high rates of polarisation a second peak produced by further reduction of the radical is detected[111]. From the nature of the I_p and V relationships observed in a study of the catalytic currents of cystine, cysteine, and albumin in the presence of cobalt ions, it was found that the magnitude of the catalytic effect is determined not only by the rate of the catalytic reaction but also by the rate of decomposition of the active complex[112].

It was noted above that the ohmic potential drop in the cell distorts the shape of the oscillopolarograms, that is it influences I_p, E_p, and their dependence on V, so that the determination of the kinetic parameters of the electrode reaction from these curves is impossible. Moreover, the non-compensated capacity current makes it impossible to use experimentally the high rates of change of potential which are often necessary for kinetic measurements. This is the reason for the comparatively small extent to which oscillopolarography is used in the study of the mechanism of electrode processes. A considerable restriction in the use of Eqns. (1)–(17) is caused by the phenomenon of adsorbability (particularly of organic depolarisers), which was not taken into account in the theoretical derivation of Eqns. (1)–(17). Oscillographic polarography can be used, however, to make a special study of the adsorption of organic compounds on

an electrode surface[1,113] and in some instances to estimate the contribution which it makes to an electrochemical process.

For substances which are not depolarisers, the method is based on the study of the change in I_C when these substances are added to the polarographic solution at different values of V. The principles of the method have been discussed[1,113]. Delahay believes[114] that the method gives erroneous results if allowance is not made, where necessary, for the fact that the adsorption is controlled by diffusion. Moreover, the method is restricted to the range of comparatively concentrated solutions of background electrolyte (greater than 0.1 M), since it does not allow for the resistance of the solution in the cell. The analytical application of this method is well known[1]. In addition to the quantitative determination of adsorbed substances from appropriate calibration curves, which generally have the form of the Langmuir isotherm, the method makes it possible to reach conclusions regarding the nature of the surface-active substances and some of their properties. The adsorption peaks with the form of a sharp maximum are characterised by a ratio $\lg I_p/\lg V$ equal to 1 (the so-called "Semerano coefficient"[65]). The situation is more complicated when the substance exhibiting surface activity is a depolariser. In this instance oscillographic polarography makes it possible to determine the adsorbed quantity of reacting substance by integration of the oscillopolarogram[115]. The integration is carried out in different ranges of potential, and for each range of integration, graphs are constructed giving the dependence of Q the quantity of electricity passed on $V^{-1/2}$. For reversible processes with only one electrochemical stage and with depolariser supplied by diffusion, this dependence is given by a straight line passing through the origin of coordinates. If reduction of the adsorbed depolariser takes place at the electrode, the straight line obtained by plotting Q against $V^{-1/2}$ has an intercept on the ordinate axis (that is as $V \to \infty$) corresponding to the quantity of electricity Q consumes in the reduction of the depolariser on the electrode surface. This method of extrapolating the values of Q to $V \to \infty$ is based on the fact that for volt-ampere oscillopolarograms of reversible processes, the current at each point of the curve is proportional to $V^{1/2}$. Comparatively recently, it was shown[116] that for irreversible processes, the area of the initial sections under the current–potential curves is independent of V (since in these regions I is determined by the rate of the actual irreversible electrochemical reaction), so that in these instances the observed dependence of Q on V is more complex, and this makes the correct extrapolation to $V \to \infty$ difficult. This method was used to study the reversible reduction of adsorbed chloranilic acid[117]. One can agree with the view[118] that this method has no advantage over the charging-curves method. To achieve the accuracy given by the recording of the charging curves, volt-ampere polarography makes more rigorous demands on the apparatus and the conduct of the experiment than the charging-curves method.

The theoretical influence of various factors on the form of the oscillopolarograms for processes involving an adsorbed depolariser has been studied by a number of workers.

When depolariser species are adsorbed, the potential–current curves after the maximum show a current drop which is much sharper than that for diffusion-limited processes, and the transfer coefficient, according to Semerano[65], is greater than 0.5. In actual fact, for diffusion limitation the current decreases comparatively slowly with time, as the diffusion layer becomes broader, in proportion to $t^{-1/2}$. On reduction of a substance in the adsorbed state, however, higher values of the currents are observed at the peak, and this is followed by a sharp decrease in the current as a result of the exhaustion of the adsorbed depolariser to a level corresponding to its rate of supply by diffusion from the depth of the solution.

Wopschall and Shain[119,120] recently studied the form of the volt-ampere curves for the reversible reduction of a depolariser with strong and weak adsorption of the depolariser on the electrode surface in accordance with Henry's or Langmuir's relationships. The curves obtained with a linearly-polarising voltage of triangular form were studied. The theoretical curves for the system without complication by adsorption are compared with those with adsorption of the depolariser or the product of its reduction in Fig. 2. Weak adsorption of the depolariser leads to a slight increase in the height of the cathodic peak relative to the system without complication, and to a smaller increase in I_a on the anodic branch of the curve.

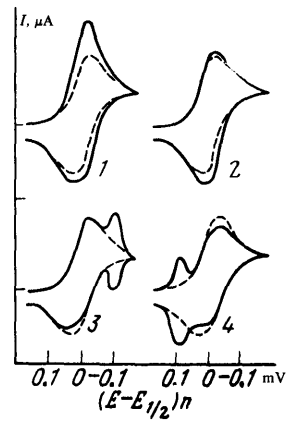


Figure 2. Theoretical forms of the oscillopolarograms for reversible electron transfer, complicated by adsorption[119]: *1*) weak adsorption of depolariser; *2*) weak adsorption of reduction product; *3*) strong adsorption of depolariser; and *4*) strong adsorption of its reduction product. The broken lines correspond to the systems not complicated by adsorption.

It is suggested that the dependence of the currents I_k and I_a on V and C_0 be used as diagnostic criteria. For high values of V the quantity of substance diffusing is small compared with the quantity of adsorbed substance reacting on the electrode surface, and for high values of V the opposite applies. Thus with increase in V the current increases relative to the value characteristic of the diffusion process for a given V. Fig. 3 gives a graph showing the dependence of the ratio of the current function Ψ (with adsorption of the depolariser) to the value 0.446 (for the process with complication by adsorption) on V. Change in the rate of polarisation also influences the magnitude of the reversible anodic peak, although its increase relative to the peak without complication by adsorption is slightly smaller than that for the cathodic peak (because of partial diffusion of the reduction product into the depth of the solution during the scanning of the polarisation pulse).

Increase in V, however, leads to a decrease in this loss of substance from the electrode surface, and the current also increases more rapidly relative to the process not complicated by adsorption. The graph giving the dependence of the ratio I_a/I_k on V has the form shown in Fig. 4, from which it can be seen that at low values of V the fraction of the current depending on adsorption becomes insignificant, and the ratio $I_a/I_k = 1$, as for the simple process. The observation that adsorption has a smaller influence on the form of the curves and the height of the peak at low values of V is a general feature of oscillopolarography, so that to decrease the effect of adsorption it is necessary to use low values of V. For weak adsorption, the fraction of the current corresponding to the adsorbed depolariser decreases with increase in C_0, and at high values of C_0 the current function Ψ takes values which are the same as those for the process without the adsorption of depolariser: this is illustrated in Fig. 5. To observe these effects, however, it is necessary to change C_0 by three orders of magnitude, and this is not always possible.

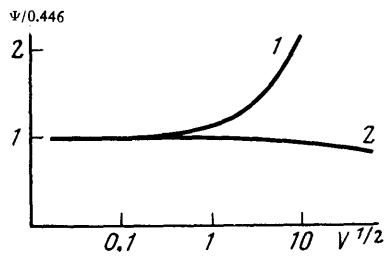


Figure 3. Dependence of the function $\Psi/0.446$ for the cathodic peak on V for weak adsorption of depolariser (*1*) and its reduction product (*2*) [119].

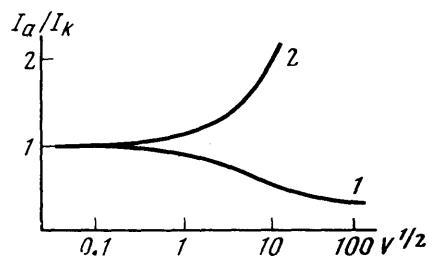


Figure 4. Dependence of the ratio I_a/I_k on V for weak adsorption of depolariser (*1*) and the product of its electrode reaction (*2*); duration of polarisation pulse after the half-wave potential $180/n$ mV [119].

An increase in the height of the anodic peak for an adsorbed reduction product relative to the peak in the absence of adsorption is usually observed when the product of the electrode reaction has been unable to diffuse into the volume of the solution during the scanning of the polarisation pulse. If the rate of polarisation is low, part of the substance is lost from the electrode surface during the passage of the pulse between the cathodic peak and the start of the anodic process, and this influences the depth of the anodic peak. This time depends on the amplitude of the pulse, so that the magnitude of the latter must be taken into account in measurements of this kind. For weak adsorption of a reducing agent, according to Wopschall and Shain[119], the cathodic peak, is only slightly displaced towards more positive potentials with increase in V, whereas the depth of the anodic peak increases appreciably and the ratio I_a/I_k also increases (see Fig. 4).

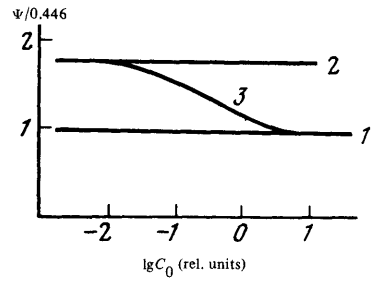


Figure 5. Dependence of the cathodic function $\Psi/0.446$ on C_0 for a system not complicated by adsorption (*1*) and for adsorption of the depolariser according to Henry's law (*2*) and Langmuir's law (*3*) [119].

At the same time, Wopschall and Shain[119] examined the case of *strong adsorption* of the depolariser or the product of its reversible electrode reaction, obeying the Langmuir isotherm.

If the product of the electrolytic reduction is strongly adsorbed on the electrode surface, the oscillopolarograms show two peaks. The first peak is an adsorption peak (its current is I_{ads}), and the second is associated with the supply of depolariser species to the electrode by diffusion (I_d) (see Fig. 2). The difference in the potentials of these peaks ΔE depends on C_0 and to some extent on V, but is determined chiefly by the nature of the adsorbed species. For low values of C_0, the ratio I_{ads}/I_d is less than 1, and the adsorption parameters are found from the half-width of the adsorption peak, ΔE for the peaks, and the dependence of I_{ads}/I_d on V and C_0. For high values of V, the preliminary adsorption peak may have diffusion character, and the diffusion peak, that is I_d, may be absent. A more detailed treatment of this example of adsorption can be found in the original paper[119].

Independently, Laviron[121] examined the influence of the adsorption of depolariser on the form of the oscillopolarograms for the reversible transfer of electrons for the example of the reduction of Methylene Blue. For $C_0 < C_{max}$, where C_{max} is the depolariser concentration at which saturation of the electrode surface takes place and the current at the peak is no longer dependent on the concentration, I_p is given by the expression

$$I_p = 6.96 \cdot 10^5 \cdot A \cdot n^2 \cdot V \cdot C_0 D^{1/2} \cdot t_1^{1/2} \qquad (18)$$

where t_1 is the time, given by the arrest before the polarisation pulse and the duration of its scanning before the peak. For $C_0 > C_{max}$, that is when the current at the

peak corresponds to the limit of the Langmuir isotherm, the value of I_p is given by the equation

$$I_p = 9.4 \cdot 10^5 \cdot A \cdot n^2 \cdot V \cdot \Gamma_{max} \quad (19)$$

where Γ_{max} is the quantity of substance adsorbed on the electrode surface. Laviron's equations, derived theoretically[121], make it possible in a number of instances to calculate the adsorption characteristics from the magnitude of the currents at the oscillographic peak.

A theoretical and experimental study of the influence of adsorption on the form of the curves for compounds undergoing irreversible reduction was made for the example of 1,2-dipyridylethylene[122]. Laviron based this study on the same premises and the assumptions[121] that the adsorption equilibrium at the electrode is displaced towards the adsorbed form of the depolariser, that is that the rate of adsorption is high and is not limited by the rate of formation of the film (at all concentrations). In this instance the current at the peak is given by the expression

$$I_p = 1.38 \cdot 10^6 \cdot n(\alpha n_a) \cdot A \cdot \Gamma_{(t_1)} V \quad (20)$$

where $\Gamma_{(t_1)}$ is the quantity of substance adsorbed in time t_1 (see above). The potential at the peak is displaced by an amount $0.059/\alpha n_a$ (at 25°) with change in V by one order of magnitude. Laviron's relationships[122] can be used to determine various parameters of the electrochemical reaction from the form of the peak.

It has been found for *m*-substituted nitrobenzenes that the current at the peak and the rate coefficient for the nitro-group depends on the nature of the substituent in the nitrobenzene molecule[64]: the higher the observed peak, the sharper the decrease in the current after the maximum (sometimes as far as the background current) and the greater the Semerano coefficient. The wave for the nitro-group appears on the curves in a range of potentials extremely favourable for adsorption. The changes in I_p, the form of the curves, and $\lg I_p/\lg V$ take place in parallel with the change in the depression of the differential capacity of the electrode in the presence of various nitro-compounds. The difference in the adsorbability of *m*-substituted nitrobenzenes is attributed to structural factors, and also to differences in the solubilities of the substances. The series studied show a tendency for I_p and $\lg I_p/\lg V$ to increase with decrease in the solubility. Analogous relationships were observed for various hydrazones[64], for which the irreversible four-electron wave appears on the curves in a wide range of potentials from −0.4 V to −1.4 V, depending on the nature of the substituent. As the reduction potential approached the point of maximal adsorption with the introduction of substituents facilitating discharge at the electrode, the peak mm on the oscillopolarogram became sharper, and the current at the peak increased, but $\lg I_p/\lg V$ exceeded 0.5, and this took place in parallel with the increase in the depression of the differential capacity. The form of the peak and the rate coefficient are also influenced by the concentration of depolariser[64,117]. In some instances the curves for a given depolariser may show two reduction current components: a surface component—a sharp peak, and a volume component—with a diffusion drop. Each of these components of the current has its own characteristic Semerano coefficient[64,117]. These phenomena on the oscillopolarograms agree with the theoretical ideas of Wopschall and Shain[119].

The adsorbability of substances on the electrode surface also explains the slight increase in the current at the peak with increased duration of the arrest before the application of the polarisation pulse, and the displacement of the initial level of recording of the curve away from the peak; this is particularly noticeable at low values of C_0. It should be noted that volt-ampere oscillopolarograms are generally recorded under conditions in which adsorption equilibrium at the electrode is not established. Adsorption with control by diffusion is retarded for strongly adsorbed substances at low volume concentrations. Convection, that is mixing of the solution, increases the rate of this process. A considerable time is sometimes necessary for equilibrium to be established (up to tens of minutes, for example in Ref. 50). Slow attainment of equilibrium at the electrode is apparently the reason for the production of hysteresis loops on current–potential curves[64]. Recently, Kalvoda[123] also emphasised that is it necessary, in the analysis of solutions with low concentrations of substances, to take account of the possibility that the establishment of adsorption equilibrium at the electrode is slow. Adsorption phenomena have also been discussed by Hale and Greef[124].

III. ANALYTICAL APPLICATIONS OF OSCILLOGRAPHIC POLAROGRAPHY

Modern forms of oscillographic polarography have developed towards an increase in sensitivity and resolving power in the study of chiefly inorganic materials. In the practical application of oscillopolarography in the last twenty years the greatest emphasis has been on the study of various ions in solution. As a result of the development of APB, oscillographic polarography has had to give some ground in inorganic analysis, since the APB method is more sensitive, and the apparatus is simpler. As already noted, however, the APB method has only a limited range of practical applications in the analysis of organic compounds, and in this field, among various electrochemical methods for the determination of small concentrations of organic substances, oscillographic polarography has recently found some applications.

1. Inorganic Analysis

The largest number of papers deal with the study of oscillopolarographic behaviour and the development of methods of determination in solution for ions undergoing reversible reduction at a d.m.e. Thus the influence of various factors on the nature of the electrochemical reduction of cadmium ions has been studied. The influence of the nature of the background electrolyte on the height of the peak for cadmium[125,126] in neutral solutions has been established. In the presence of halide anions and a trace of oxygen, the $I = f(E)$ oscillopolarogram in the potential region for the reduction of Cd^{2+} contains two peaks instead of one[125]. The explanation for the production of the peak at more negative potentials is that some of the Cd^{2+} ions at the electrode combine with OH^- ions (formed by the reduction of O_2) to form the sparingly soluble hydroxide, which is adsorbed by the electrode and subsequently reduced. The addition of gelatin or methylcellulose leads to a decrease in the height of this peak, until it disappears completely. The peak is also eliminated by acidification of the solution. This peak has been described as an oxygen peak[126], and it was later shown that its production requires a reaction taking place in parallel with the discharge of cadmium ions and bringing

about the electrochemical generation of OH^- ions. Study of the simultaneous reduction of cadmium ions and bromate anions at a d.m.e. by means of multi-cycle oscillographic polarography with a linearly changing potential[126] showed that the discharge of bromate ions can provide a source of hydroxide ions. Subsequently, a direct proportionality was established[127] between the height of the cadmium peak and the pH of the solution in the pH range 4–6.4. Thus in the presence of O_2 the sensitivity of the determination of Cd^{2+} depends on pH. Cadmium, lead, and thallium, which react reversibly at the electrode, have been the objects of a large number of studies by volt-ampere oscillopolarography. The chief results are summarised in the Table.

Oscillopolarographic study of inorganic ions at a mercury electrode.

Ion	Materials studied and conditions of polarography study	Results obtained	Refs.
1	2	3	4
Cadmium	Ammonia–ammonium salt buffer	Influence of V on reduction	128
	Halide solution	Influence of the nature of the background ion on the rate coefficient, the role of adsorption, and the mechanism of reduction	63
Cadmium and zinc	1 M NH_4Cl, 4 M NH_4OH in the presence of atmospheric oxygen	Selection of optimal conditions for analysis	129
Cadmium, thallium, and zinc	1 M KNO_3 and 0.9 M ammonia–ammonium salt buffer	Influence of V on an assembly with sinusoidal voltage in the range 100–200 V s^{-1}	130
Cadmium, thallium, copper and zinc	1 M CH_3COONH_4, 1 M acetate and ammonia–ammonium salt buffer	Study of the form of the reduction curves at an amalgamated silver electrode	131
Cadmium	1 M ammonia–ammonium salt buffer and Na_2SO_3	Rapid determination in the presence of copper	132
	Present together with lead and zinc in a 5000-fold excess of copper	Determination by differential oscillopolarography, resolving power ~30 mV	133
	Pure salts KCl, NH_4Cl, K_2SO_4, KI, KNO_3, KSCN, and $K_2C_2O_4$	Determination by an oscillopolarographic version of amalgam polarography with build-up	134
	Zinc electrolyte	Simultaneous determination of cadmium and nickel	135
Cadmium, lead, and zinc	4 M ammonia–ammonium salt buffer	Amperometric titration with Complexone III on an oscillopolarograph	136
Lead	1 M NH_4Cl	Selection of optimal conditions for analysis	129
Lead	1 M KNO_3 in the presence of atmospheric oxygen, buffer solutions	Influence of V on ΔE_{pak}; change to irreversible reaction with increase in pH; two forms of ion in solution $PbOH^+$ and $HPbO_2^-$	130
	Lead in bismuth without removal of O_2	Bismuth does not interfere in the determination of lead as far as a ratio Pb : Bi = 1 : 300	137
Bismuth and lead	Lead and bismuth in copper-based alloys	Determination of small quantities	138
Lead	In sea water and the basic rocks of the Pacific volcanic belt	Determination of small quantities	139,140
	In titanozirconate ceramic	Determination of small quantities	141
	In water, petrol, and biological materials	Determination by differential oscillopolarography	142
Lead	In blood	To 0.1 γ in 20 ml solution	143

Table cont'd.

Ion	Materials studied and conditions of polarography study	Results obtained	Refs
1	2	3	4
Thallium	In the presence of atmospheric oxygen, cobalt, and manganese	Quantitative determination	144
Fe^{3+}/Fe^{2+}	0.4 M H_2SO_4	Influence of V on the form of the curves at a Pt electrode	145
	Pyrophosphates in the presence of titanium and copper	Quantitative determination	146
Fe^{2+}	Mixed complexes with bipyridyl and phenanthroline and acetonitrile	Determination of adsorption-kinetic factors in electrolytic reduction	147
	Sulphuric acid medium	New method of coulometric study at Pt and Au electrodes down to ~10^{-7} M	148
Copper and antimony	In the presence of bismuth, cadmium, lead and zinc	Determination of down to 10^{-6} M by difference oscillopolarography	15
Zinc	In the presence of a 290-fold excess of nickel, 690-fold excess of cadmium, and 3580-fold excess of copper	Determination of down to ~3×10^{-6} M by difference oscillopolarography	15
Antimony	1 M HCl	Oscillopolarographic characteristics of the reduction	87
	In cast iron, 6 M HCl	Quantitative determination	149
	6 M HCl	Traces down to 0.1 γ in 1 ml	150
Bismuth	Semiconducting alloys, potassium chloride and oxalic acid in the presence of a 100-fold excess of tin	Quantitative determination	151
Copper and lead	In the presence of sulphonic acid derivatives of 8-quinolinol	Determination of down to 0.013 γ and 0.2 γ in 1 ml respectively	152
Cobalt and nickel	In nickel and cobalt	Quantitative determination	153
Nickel	In cobalt salts, saturated $CaCl_2$ solution without removal of O_2	Quantitative determination	154
Nickel, cobalt, zinc	Pyrophosphate background	Selection of conditions for analysis	155,156
Aluminium	In thorium compounds, in the complex with 2,2,4-trihydroxyazobenzene-5-sulphonic acid	Quantitative determination of down to fractions of 1 γ	157
	In solutions of complex-forming salts	Oscillographic behaviour	158,159
Copper, silver, gold	In the presence of chlorides, thiocyanates, ammonia, pyridine, ethylamine, 2-aminoethanol, 2,2'-2"-nitrilotri(ethanol), piperidine and ethylenediamine	Study of complex formation and selection of conditions of analysis	160
Palladium, copper, gold	In alloys	Quantitative determination	160
Gold, silver	In gold coatings on molybdenum and tungsten, in plant ash, in pure antimony	Determination of ultra-small quantities with preliminary concentration at a carbon paste electrode	161,163
Palladium	In the presence of a 70-fold excess of copper	Quantitative determination	162
Ruthenium, rhodium, palladium, osmium, iridium	In solutions of chloride, thiocyanates, cyanides, ammonia, and pyridine	Study of the electrolytic reduction of complexes, selection of conditions for the analysis of ruthenium, rhodium, and palladium in alloys	164
Niobium	In titanozirconate ceramic, in titanium–niobium and tantalum–niobium alloys, 23 N H_2SO_4	Quantitative determination	141,165, 166
Titanium	In titanozirconate ceramic, in sodium pyrophosphate solution, in the presence of uranium, in phosphoric acid media	Quantitative determination	141,167, 56,168

Table cont'd.

Ion	Materials studied and conditions of polarographic study	Results obtained	Refs
1	2	3	4
Uranium, molybdenum	In the presence of a 10-fold excess of Ferron (7-iodo-8-quinolinol-5-sulphonic acid)	Simultaneous quantitative determination	169
Vanadium	Mineral acids, ammonia-ammonium salt buffer	Study of the multi-stage nature of the reduction $V^{V} \rightarrow V^{II}$; separate stages almost reversible	130,170
Tungsten	7 M hydrochloric acid	Selection of conditions for analysis, use of second peak for reduction of tungstate anion	171
ReO_4^-, $ReCl_6^{2-}$	1-11 M hydrochloric acid	Study of stepwise reduction	172-174
Europium, ytterbium	Monazite sand, background containing ammonium salts and hydrazine	Study of the influence of the composition of the background on the form of the curves, quantitative determination	175
Samarium, dysprosium, ytterbium, lutetium, lanthanum, praseodymium, terbium	Various mineral acids, lithium chloride	Determination of the pH of the start of precipitation of the hydroxides, oscillopolarographic characteristics of the reduction, quantitative determination in phosphors	176-185
Scandium	Lithium chloride acidified with hydrochloric acid	Irreversible reduction at Au, Ag, Ni electrodes, scandium discharge peak follows hydrogen ion discharge	186
Germanium	In solutions of halides, sulphates, carbonates, phosphates	Quantitative determination of Ge^{IV} in 1 M NH_4Cl in the presence of Complexone III	188
	Semiconducting materials, in the presence of selenium, tin, and zinc, alkali solutions with pH ~ 12 in the presence of oxalate anions	Quantitative determination	189-191
Gallium	Semiconducting alloy, 0.2 M alcoholic solution of tetraethylammonium iodide	Quantitative determination of tenths of 1% gallium	192
Tellurium	Hydrochloric and sulphuric acids	Oscillopolarographic characteristics of reduction, second peak used for analysis, 100 times greater than first	193
Uranium	Concentrated phosphoric acid	Determination of down to ~4×10^{-7} M	194
Oxygen	In aqueous solutions, in petrol	Study of oscillopolarographic behaviour, quantitative determination	195,196
Boron	B-Si-C alloys, in a solution of orthoboric acid, sodium sulphite, and mannitol	Determination as mannitol-boric acid	197
Sulphur	In petroleum products, background of 0.04 M sulphuric acid in ethanol	Quantitative determination of aggressive sulphur (S and H_2S) at flowing mercury and Ag electrodes	198
Halogens	In solutions of potassium halides and nitrate	Quantitative determination at an Ag electrode	199
Sulphur, arsenic, and phosphorus anions	Neutral salts and alkaline solutions	Study of oscillographic behaviour, selection of conditions for direct and indirect determination	200-203

The material presented has dealt with the study of various elements in solution. In combination with solid electrodes, however, the method of oscillographic polarography has also been used to study salt melts [204-207]. Silver, lead, and cadmium chlorides have been studied in an equimolar mixture of potassium and sodium chlorides in the range 700-900° [207]; the results confirmed the earlier conclusion [205] that oscillographic polarography can be used for rapid quantitative analysis in molten salts.

The reduction of silver ions in an LiCl-KCl eutectic melt at 500° at low rates of application of the voltage at a platinum cathode [205], and the behaviour of cadmium, lead, tin, and copper ions in an $AlCl_3$-NaCl melt in the range 150-230° at a d.m.e. [208] have also been studied. The behaviour of halide anions was studied in a molten sodium nitrate-potassium nitrate eutectic with stationary and dropping mercury electrodes in the range 230-270° [209]. It was shown that in spite of the fact that the products of the oxidation of these anions at the electrode react with nitrates, distorting the form of the oscillopolarograms, their quantitative determination in the melts is possible.

2. Analysis of Organic Compounds

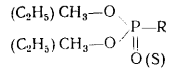
By means of classical polarography it is possible in principle to determine ~10% of all organic substances containing a polarographically active group in the molecule, whereas by means of oscillographic polarography it is possible to analyse not only these compounds but also those which in solution alter the capacity of the electrode double layer. As with inorganic materials, most papers on organic oscillopolarography have been devoted to the study of the behaviour of compounds under different conditions, the influence of the latter on the form of the oscillopolarograms, and the development, on the basis of these results, of specific methods of analysis.

Among organic compounds containing a nitrogen atom in the molecule, detailed studies have been made of the irreversible oxidation of a number of primary, secondary, and tertiary aliphatic amines at a platinum electrode in acetonitrile in a background of $NaClO_4$ [210]. The difficulty of oxidation increases on going from tertiary to secondary and primary amines. Oscillographic studies at a d.m.e. have also been made for hydrazine and hydroxylamine in alkali solutions [211]; the results, however, did not make it possible to reach an unambiguous conclusion regarding the nature of their anodic peaks; they are associated either with oxidation of the substance at the electrode or with reaction with mercury.

Detailed studies have been made of organic compounds containing sulphur, in particular thiourea and its derivatives [52,212], and various thiols [53,213]. The oscillograms for thioacetamide, thiourea, diphenylthiourea, thiosemicarbazide, and dithizone give a sharp cathodic peak, with adsorption characteristics, over a wide pH range. Its height depends not only on the concentration of depolariser, but also on the initial potential of polarisation of the mercury electrode, since it is associated with the formation of a film of an intermediate compound of thiourea or its derivative with mercury. This intermediate compound is capable of undergoing hydrolysis with the formation of mercury sulphide, corresponding to the same cathodic peak on the oscillopolarograms. A peak with analogous form and properties was also observed on the oscillopolarograms of thiols: thioglycollic and thioacetic acids, sodium thioglycollate, cysteine, etc. [53,213,214]. Various S-methyl-substituted thioureas in alkaline solution also gave a cathodic peak similar to the thiol peak [52]. The latter is due to the reduction of mercury thiolate, produced by the reaction of the thiols with mercury on the electrode surface. The works cited [213,214] also describe the oscillopolarographic behaviour of substances containing thiol and thione groups simultaneously in the molecule, such as sodium diethyldithiocarbamate, K ethyl xanthate, and di-isopropyl xanthate disulphide. Their behaviour in alkaline and acidic media resembles that of thiourea and its N-substituted derivatives. Almost no differences are observed in the form of the curves for K ethyl xanthate

and sodium diethyldithiocarbamate in acid solutions, since under these conditions the compounds decompose with the formation of carbon disulphide, which is responsible for the electrochemical activity of the polarographic solution. The works cited[52,53,212-214] consider the possibility of using oscillographic polarography to determine the following organic compounds in their mixtures with one another: thioglycollic acid and thiourea, K ethyl xanthate and sodium diethyldithiocarbamate, and K ethyl xanthate and carbon disulphide, in strongly alkaline or acidic solutions.

As noted above, many organic substances are not reduced or oxidised, but nevertheless give sharp peaks on the oscillopolarograms, due to a sharp change in the capacity of the electrode. Peaks of this kind were found to be characteristic of most organophosphorus compounds used as insecticides, and can be used for quantitative determinations at concentrations of 3×10^{-7} M [215]. The work cited[215] describes a study of dimethyl and diethyl esters of phosphoric and thiophosphoric acids with the general formula



where R represents various alkyl, aryl, or mixed substituents, in a medium of water and organic solvent (CH_3OH, C_2H_5OH, and CH_3COCH_3) in the ratio 1 : 1, with 0.2 M HCl, KCl, or NaOH solutions as background. It was noted that the peaks on the curves are more stable with time for the thio-analogues than for the phosphates and more stable in HCl or KCl than in alkali.

The behaviour under the conditions of oscillographic polarography has been studied for the semicarbazones and thiosemicarbazones of carbonyl compounds[216], the phenylhydrazones of pyruvic aldehyde and ethyl diketobutyrate[217], 5-nitromucic acid and its methyl ester[218], various compounds containing nitro and azomethine groups in the molecule[64], the azo dye Eriochrome Black[219], nitro- and aminoterephthalates[220], the nitriles of acrylic, vinylacrylic, and cinnamic acids[105], the organic analytical reagents 1-nitroso-2-naphthol[221], disodium 1-nitroso-2-naphthol-3,6-disulphonate[222], Cupferron[107], and various heterocyclic compounds: indolizines[223], aminobenzothiazoles[224-226], pyrazine[227], derivatives of 4,4-bis(triansylamino)stilbene-2,2-disulphonic acid[228], and pyrimidones[229].

The study of the behaviour of organic substances under the conditions of oscillographic polarography, described in Refs. 216, 218, and 227, and more particularly Ref. 64, has shown that the form of the curves for organic depolarisers in general depends on their concentration, the pH of the solution, the nature of the solvent, and the concentration of the background electrolyte. The fact that the form of the oscillopolarograms depends on the conditions of the polarographic study and the concentration of the depolariser, which is not always known in analysis, casts doubt on the effectiveness of the use of the so-called oscillopolarographic atlas for the identification of organic substances. This atlas[230] was based on the assumption that the form of the oscillopolarogram is specific for a given substance or series of structurally related substances, and has been proposed for the qualitative detection of organic depolarisers.

Oscillographic polarography has also been used for quantitative determinations in the analysis of α,β-unsaturated ketones present in technical methyl isobutyl ketone[231], various substances exhibiting the properties of photographic developers, such as hydroquinone, *p*-aminophenol[232,233], phenidone[233], substances acting as sensitisers[234,235], and tetraethylthiuram disulphide in the presence of elementary sulphur in organic extracts[236]. Various versions of the use of one-pulse and multi-pulse oscillographic polarography for the analysis of developers, stabilisers, and colour developer components in photography, and polyethylene glycols, which are chemical stabilisers in the production of cinephotographic materials, have been discussed[234]. In the last example an empirical relationship was established between the surface activity of the substance, and hence the height of the adsorption–desorption peaks on the oscillopolarograms, and the molecular weight of the polyethylene glycols.

A study of the oscillographic behaviour of various organic dibasic acids with the general formula $HOOC-(CH_2)n-COOH$, where $n = 0, 1, 2, 3$, or 4, showed that acids such as oxalic, malonic, succinic, and adipic in a background of $NaClO_4$ in the presence of Ge ions give distinct reduction peaks on the oscillopolarograms. Germanium itself is inactive in weakly acidic media, and its presence does not interfere in the analysis, but on the contrary increases the height of the peak for the dicarboxylic acid as a consequence of its catalytic action on discharge at the electrode.

The heights of the peaks depend on the concentration of catalyst depolarisers, the buffer capacity and acidity of the solution, and the nature of the indifferent electrolyte. It was found that with increase in the number of CH_2 groups in the organic acid molecule in the series malonic–succinic–adipic there is a gradual decrease in the catalytic peak and its potential is displaced towards more negative values[237].

Oscillographic polarography has been used successfully for the quantitative analysis of the three stereoisomeric forms of 1,4-distyrylbenzene in the presence of one another[238]. On classical polarograms these stereoisomers give waves with similar values for the half-wave potentials. If the differential oscillopolarograms are recorded, however, the selective determination of the *cis-cis* and *cis-trans* isomers in the mixture becomes possible (the *trans-trans* isomer is separated as a consequence of its low solubility in the polarographic medium) with the condition that the relative concentration of the *cis-cis* form does not exceed 75–80%.

It should be noted that the analysis of organic compounds by oscillographic polarography exhibits a number of specific features, which have been partly discussed above. The adsorbability of the depolariser species on the electrode surface explains the production of two components of the reduction current—the surface component (sharp peak) and the volume component (with a diffusion loop)[64,117]. Since oscillographic polarography exhibits a fairly high resolving power with respect to potentials (this increases for processes involving the adsorption of depolariser species), the form of the curves in the last instance can lead to the erroneous conclusion that the solution contains two electro-active substances. These characteristic features of the behaviour of organic substances under the conditions of oscillographic polarography must be taken into account in the development of analytical methods involving its use.

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The development of modern radioelectronics has made it possible to create a wide range of new techniques

in oscillographic polarography, and these have greatly extended the range of practical applications of the method.

It should be noted, however, that each of the methods has its disadvantages and limitations[4]. Those methods which provide promising possibilities in analytical chemistry are particularly noteworthy. These are primarily the method involving fractional differentiation of the oscillopolarographic curve, which makes it possible to eliminate intermediate diffusion components, and hence to alter its form in appropriate fashion; the method involving automatic and controlled compensation of the volume resistance of the solution, which makes possible the polarographic study of non-aqueous solutions; and the method involving a stepped polarising voltage, which eliminates the influence of the background current. It should be noted that oscillographic polarography with triangular scanning of the voltage has a definite advantage over the method involving a saw-toothed form of polarising voltage, since it makes it possible to obtain information on the cathodic and anodic processes simultaneously.

The main achievements of oscillographic polarography are associated not only with the development of new methods of measurement. The development of methods for increasing the sensitivity, based on the adsorption of depolariser species, the action of various salting-out agents, or other means of concentrating the substance being determined on the electrode surface shows that the possibilities provided by oscillopolarography are not yet exhausted. The importance of studying the various factors which determine the form of the oscillographic polarograms and which must be taken into account in the qualitative and quantitative analysis of solutions should also be noted.

Review of published work shows that oscillographic polarography can be used successfully to study electrochemical processes complicated by fast chemical reactions taking place together with transfer of electrons to the depolariser. The interpretation of the oscillopolarograms obtained for this purpose for organic compounds which can be adsorbed on the electrode surface is complicated, however, and further work in this direction is required.

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