DISTINGUISHING SOME TYPES OF ONE-ELECTRON REVERSIBLE PROCESSES ACCORDING TO DIFFERENT POLAROGRAPHIC WAVE FORMS

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Received May 28th, 1981

Based on different shapes of polarographic one-electron waves influenced by preceding or follow-up dimerization reactions, a computational diagnostic method for distinguishing various types of the corresponding reaction mechanisms was elaborated, based on approximate relations between current and applied voltage. It enables one to evaluate statistically the distinguishing of a simple reversible reduction from a reduction accompanied by a rapid dimerization either in the adsorbed state on the electrode or in its vicinity. Factors influencing the selectivity of the method are discussed.

Logarithmic analysis of classical polarographic curves is a diagnostic means for obtaining information about the number of transferred electrons or the degree of reversibility of an electrochemical reaction. If we study a series of chemical analogues, the slope of the logarithmic dependence suggests a similarity or dissimilarity of the electrode processes involving the individual compounds under study.

The condition for a significant information is, of course, that the logarithmic dependence of the current on the voltage be linear at least in the range from 10 to 90% of the wave height. If this is not the case and if overlapping of the reduction waves of differently protonated forms[1] can be excluded (provided that considerable experimental errors are absent), then the deviation from the linear course can be attributed to a rapid chemical reaction participating in the electrode process, especially in the case of a one-electron reduction. If the latter leads to the formation of a radical, we can assume its rapid dimerization or dismutation either in the adsorbed state on the electrode or close to its surface.

Kastening[2] with reference to Koutecký and Hanuš[3,4] gives in his review about free radicals in organic polarography approximate equations of polarographic curves influenced by a chemical reaction participating in the electrode process. The use of these equations for diagnostic purposes was greatly facilitated by the modern computation techniques enabling one to analyse curves obtained with complicated systems with regard to experimental errors and with a statistical evaluation of the reliability of the obtained results.

We attempted in the present work to determine the character of the electrode process in the case of one-electron waves from their deviations from the symmetrical form.

THEORETICAL

In the case of a simple reversible reduction on the dropping mercury electrode, the current is governed by the Heyrovský–Ilkovič equation, which can be written in the form

$$\frac{1 - i/i_{\text{lim}}}{i/i_{\text{lim}}} = \exp \frac{nF(E - E_0)}{RT}, \tag{1}$$

where i denotes the mean current due to reduction of the studied depolarizer at an applied voltage E, i_{lim} limiting diffusion current, E_0 redox potential of the depolarzer, n number of transfered electrons ($n = 1$ in the case of radical formation), T absolute temperature, R gas constant, and F Faraday's constant. Analogously, we can write the approximate equation of Koutecký and Hanuš[3] for the polarographic wave corresponding to a rapid dimerization of the formed radical as follows:

$$\frac{1 - i/i_{\text{lim}}}{(i/i_{\text{lim}})^{2/3}} = \frac{1{\cdot}15}{(k_{\text{dim}}c_0\tau)^{1/3}} \exp \frac{nF(E - E_0)}{RT}, \tag{2}$$

where k_{dim} denotes dimerization rate constant for the succeeding reaction, c_0 depolarizer concentration, and τ drop time.

If the radical adsorbed on the dropping electrode undergoes dimerization, then according to Mairanovski and coworkers[5] we have the equation

$$\frac{1 - i/i_{\text{lim}}}{(i/i_{\text{lim}})^{1/2}} = \frac{1{\cdot}11}{(k_{\text{dim}}c_0 \sqrt{\tau/D})^{1/2}} \exp \frac{nF(E - E_0)}{RT}, \tag{3}$$

where D denotes diffusion coefficient of the oxidised form.

If the radical undergoes rapid dimerization, this reaction influences also the succeeding wave due to reduction of this radical. This wave is approximately given by the equation[2]

$$\frac{1 - (i/i_{\text{lim}})^{2/3}}{i/i_{\text{lim}}} = \frac{1{\cdot}07 \sqrt{D}(k_{\text{dim}}c_0)^{1/3}}{k_{e0}\tau^{1/6}} \exp \frac{nF(E - E_0)}{RT}, \tag{4}$$

where k_{e0} denotes standard rate constant of the electrode reaction.

The differences in the left sides of Eqs (*1*)–(*4*) enable us to distinguish the reaction mechanism from the wave form. Assuming that the preexponential terms are independent of the voltage,* we can linearize Eqs (*1*)–(*4*) by logarithming and compare them with experimental data.

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* Essentially, we neglect only the potential dependence of τ.

To simplify notation, we shall introduce the following symbols:

$$L_1(x) = \log [(1 - x)/x] , \tag{5}$$

$$L_2(x) = \log [(1 - x)/x^{2/3}] , \tag{6}$$

$$L_3(x) = \log [(1 - x)/x^{1/2}] , \tag{7}$$

$$L_4(x) = \log [(1 - x)^{2/3}x] , \tag{8}$$

where $x = i/i_{\text{lim}}$. In the case of an improper choice of the function $L_r(x)$, the dependence of $L_r(x)$ on the voltage E will be more or less different from a straight line.

In the text below, we shall deal with the statistical analysis of experimental data with the aim to determine the type of the reaction by evaluating the deviations of the dependence of L_r on E from a straight line.

Algorithm of General Logarithmic Analysis

The accuracy of the logarithmic analysis is influenced first of all by the mode of obtaining primary data, *i.e.*, values of voltage, E, and the corresponding mean current, i. These are usually read off from a diagram drawn by an electronic pen-recorder. The current i is then expressed in arbitrary units (usually mm) as a quantity i', which is directly proportional to i. This, however, is not manifested in the dimensionless quantity x. It can be assumed that the dispersion variance (σ^2) in evaluating the graphical record (*i.e.*, the quantity i') will not exceed 0·25 mm^2 on the average.

The value of i', read off with respect to zero line of the recorder, consists of two components: the current due to reduction of the depolarizer, i_{dep}, and the residual current, i_c, which involves the charging current and the diffusion current of other depolarizers present as impurities in the electrolyte

$$i' = i_{\text{dep}} + i_c . \tag{9}$$

The dependence of the residual current on the potential, E, is usually estimated from the record of the pure base electrolyte, whose curve is, if necessary, shifted so as to coincide with the studied curve in the potential region where the depolarizer is inactive. The limiting current is then measured against this base line. An uncertainty in determining the residual current gives rise to a systematic error which will not be considered here; this adds to the uncertainty in bringing the curve of the base electrolyte to contact with the studied curve, so that the measured values of i_{dep} are subject to a constant systematic error Δi_c. Similarly, an uncertainty in determining the potential E_{lim} at which the current attains its limiting value, combined with an uncertainty in determining the corresponding value of $i_c(E_{\mathrm{lim}})$, causes the value of i_{lim} to be subject to an error Δi_{lim}, which may be important if the potential is close to the reduction of the base electrolyte.

Therefore, in logarithmic analysis, the function $L_r(i_{\mathrm{dep}}/i_{\mathrm{lim}})$ is replaced by a more complicated one,

$$L_r[(i_{\mathrm{dep}} - \Delta i_c)/(i_{\mathrm{lim}} - \Delta i_{\mathrm{lim}})] .$$

In this approximation, we can, from the statistical point of view, consider the quantity i_{dep} in a single run as a random variable with a standard deviation σ_i; the quantities Δi_c and Δi_{lim} can be considered under these conditions as random variables with a zero mean value and standard deviations σ_c and σ_{lim} respectively. For a certain measurement, Δi_c and Δi_{lim} are unknown parameters which are to be determined so as to minimize a suitably chosen norm ("cost function") describing both the deviations of the dependence of L_r on E from a straight line and the deviations of Δi_c and Δi_{lim} from zero.

A suitable norm characterizing the linearity of the dependence of L_r on E is the sum of squares of weighted deviations of L_r from the regression line. Different statistical weights are ascribed to the different data points, since equal errors in the value of i_{dep} are after the logarithmic transformation manifested differently in the values of L_r. According to the law of propagation of errors, the dispersion variance σ_L^2 is given by the approximate equation

$$\sigma_L^2 = \mathrm{d}L_r[(i_{\mathrm{dep}} - \Delta i_c)/(i_{\mathrm{lim}} - \Delta i_{\mathrm{lim}})]/\mathrm{d}i_{\mathrm{lim}}\sigma_i^2 . \qquad (10)$$

The best choice of the weight factor is then $w(i_{\mathrm{dep}}) = 1/\sigma_L^2$; this makes the expected sum of squared deviations equal to the total number of experimental points, n, minus one.

In adjusting the unknown parameters Δi_c and Δi_{lim}, it should be kept in mind that the functions $L_r(x)$ are defined only for $0 < x < 1$, having no sense outside this interval. To prevent difficulties in the calculations, such experimental points for which the the argument of the function L_r is outside its definition interval* are disregarded in the calculation; the sum of the squared deviations is normalized back to the original number of points by multiplying with $n/(m - 1)$, where m is the number of experimental points actually considered.

As suitable norms for adjusting the parameters Δi_c and Δi_{lim}, the quantities $(\Delta i_c/\sigma_c)^2$ and $(\Delta i_{\mathrm{lim}}/\sigma_{\mathrm{lim}})^2$ were chosen, whose expected value is equal to 1; if they

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* From the practical point of view, these points may lie either at the beginning or at the end of the studied region, of the polarographic curve, either dropping below the curve of the residual current or above the considered limiting current.

are given the same weight as the sum of squared deviations, they must be multiplied with the number of experimental points, n.

The total norm is equal to the sum of the three above-mentioned norms, hence

$$S = \frac{n}{m-1} \sum (L_r - aE - b)^2 \, w(i_{dep}) + n(\Delta i_c/\sigma_c)^2 + (\Delta i_{lim}/\sigma_{lim})^2 \,. \qquad (11)$$

The expected value of the norm for a suitably chosen function L_r is in this case $3n$. If it is markedly surpassed with all studied types of functions, it can be concluded that one of the necessary assumptions is not fulfilled (the mechanism of the process is different, the background function is wrongly approximated, several waves overlap, *etc.*).

For processing of data on a computer (or on a programmable calculator), the function S was minimized by the method of moving grid[6]. For an initial estimate of Δi_c and Δi_{lim}, the dispersion variance of the functions L_r for individual experimental points is calculated from Eq. (*10*) and from them the corresponding weight factors $w(i_{dep})$. After their substitution, a straight line is led through the set of points (E, L_r) and the norm S is recalculated from Eq. (*11*). Afterwards the proximity of the point $(\Delta i_c, \Delta i_{lim})$ is examined and a better estimate of Δi_c and Δi_{lim} is sought until the minimum of the norm S is found or one of the values of Δi_c and Δi_{lim} becomes more different from zero than really possible. The χ^2 test[7] was used to check the acceptability of the chosen mathematical model.

The mentioned algorithm was written in the form of a computer program in OS level F FORTRAN IV for IBM 360/40 or IBM 370/135 and in BASIC for the desk calculator HP 9830 A. The program was formally arranged so that it required the input data for the estimated initial (i_c) and final (i_{lim}) current, couples of instantaneous current and voltage values, initial and final iteration step of the change of Δi_c and

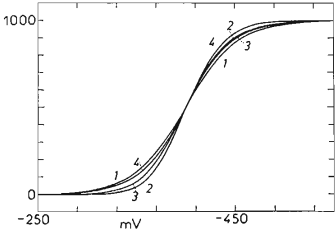

FIG. 1

Characteristic current–voltage curves at $E_{1/2} = -400$ mV for the function types *1*–*4*. Curve numbers refer to the equations, given in the text

Δi_{lim} and the magnitudes of the presumed errors σ_c, σ_{dep}, and σ_{lim} of the initial (capacitive), instantaneous, and limiting currents, respectively.

After the calculation is finished, the computer indicates the half-wave potential, the reciprocal-slope of the logarithmic dependence of current on voltage, the optimized values of the initial (i_c) and final (i_{lim}) currents, and the statistical probability of fitting the data with an arbitrarily chosen function.

Testing the Program

To verify the diagnostic value of the algorithm, polarographic curves corresponding

TABLE I

Differences between preset and optimized parameter values for simulated polarographic curves

Sought function type	Simulated function type			
	1	2	3	4
Half-wave potential $E_{1/2}$, mV				
1	+ 0·06	+ 10·69	+ 7·06	− 7·34
2	− 14·33	− 0·01	− 4·77	− 19·90
3	− 8·71	+ 4·23	− 0·04	− 14·81
4	+ 8·85	+ 17·41	+ 4·46	− 0·19
Reciprocal slope, mV				
1	+ 0·58	− 13·18	− 9·20	− 8·78
2	+ 20·53	+ 0·63	+ 6·52	+ 9·74
3	+ 12·66	− 4·68	+ 0·38	+ 2·23
4	+ 12·74	− 3·05	+ 1·66	+ 0·83
Capacity current i_c				
1	+ 0·60	+ 1·00	+ 1·15	+ 1·10
2	− 0·65	− 0·25	− 0·10	+ 1·10
3	+ 0·60	− 0·25	− 0·10	+ 1·10
4	+ 0·60	+ 1·00	+ 1·15	+ 2·35
Limiting current i_{lim}				
1	− 2·15	− 0·45	− 0·95	− 1·90
2	− 2·15	− 0·45	− 5·95	− 1·90
3	− 2·15	− 0·45	− 0·95	− 1·90
4	− 2·15	+ 0·80	− 0·96	− 1·90

to Eqs (*1*)–(*4*) were generated. The obtained data were modified by random fluctuations with a mean value equal to zero and with a determined dispersion variance $\sigma^2_{\text{dep}} = 0{\cdot}25$ at a total wave height $i_{\text{lim}} = 1\,000$ and chosen value of $i_c = 0$.

Since the kinetic and concentration parameters on the right-hand side of Eqs (*2*) to (*4*) influence only the half-wave potential, the curves were constructed with an arbitrarily chosen value of $E_{1/2}$. The data thus prepared were analysed and the recalculated value of $E_{1/2}$ and the slope of the wave were judged. The curves characteristic for the given functions are shown in Fig. 1.

DISCUSSION

The correctness of the proposed algorithm is evident from Table I summarizing the polarographic data for the simulated functions. All differences in the recalculated values of $E_{1/2}$ and wave slopes are, as expected, smallest in the case of a function given beforehand. The deviations of the $E_{1/2}$ values and slopes from the preset values are less than 1 mV in most cases; they are due to random errors generated in the set of simulated data.

The recalculated, optimized values of i_c and i_{lim} are also close to the preset ones for the simulated curve. In a number of cases, the deviation from the theory is smallest for the right type of function; in cases where a better approximation was attained with a wrong function, the difference in the i_c or i_{lim} values for the right and wrong functions was much below the experimental error limit.

For depolarizers with a known electrode reaction mechanisms, the logarithmic slope of the wave is sometimes higher than would correspond to a one-electron reversible process. The possibility of a partial irreversibility of the electrode process accompanied by a succeeding dimerization was, however, pointed out already by Koutecký and Hanuš[3].

A necessary condition for distinguishing the various reaction mechanism from a statistical evaluation of the quality of linearization of the corresponding curves is a perfect record of the studied polarographic curve. Besides deformations due to the electrode process (adsorption or overlapping of two waves), the analysis of the curve can be seriously complicated by random disturbances of the record. An error of ±1% in the current value (with respect to the limiting current) can lead in some cases to an inverted order of probabilities of the reaction types, whereas with an error of ±0·2% the statistical distinghuishing is satisfactory.

To obtain a significant logarithmic analysis, a sufficiently wide current range is necessary. According to Meites[8], the recommended range for checking the reversibility is ±1·5 of the logarithmic unit. In our case, to evaluate the wave form especially at its foot[9], a range of ±2 or rather ±2·5 logarithmic units had to be used. Thus, it was necessary to measure currents smaller than 1% of the limiting current. The required quality and accuracy of the curve can be obtained by a digital record rather than by evaluating a recorded diagram.

The sharpness of the discrimination is also conditioned by the density of sampling the current–voltage couples on the studied curve. In the case of one-electron processes, taking data at 20 mV intervals is sufficient (with elongated curves, even at 50 mV intervals). Thus, the values of $E_{1/2}$, of the slope, and mainly of i_c and i_{lim} can be rapidly estimated. The estimation of optimum values approximating the capacity and limiting currents is very important for the statistical discrimination of various curve types. When the difference between the values of i_{lim} and i_c was smaller than the true wave height, the statistical discrimination was less reliable, and in some cases even a reaction type different from the simulated one was assigned to the polarogram.

It would appear that a smaller wave height than that found experimentally cannot be used in the calculation. However, even slight differences in the preset values

TABLE II

Statistical discrimination of reaction mechanisms corresponding to real polarographic curves

Depolarizer	Solution	Stat. probability of function type				σ_c nA	σ_i nA	Reaction mechanism	Ref.
		1	2	3	4				
Tl^+	0·1M-KNO_3	99	0	0	0	1·02	2·55	reversible reduction	10
1-N-methyl-pyrimid-2-one	Britt.-Rob.-buf. pH 6·80	0	3	99	0	2·00	5·00	radical dimerizat.	11
Benzophenone	0·1M-HCl in 25% EtOH	0	99	11	0	3·37	8·43	radical dimerizat.	12
I, posit. wave	0·1M t-Bu_4NClO_4	99	0	0	0	0·94	2·35	rev. red.[a]	13
I, negat. wave	0·1M t-Bu_4NClO_4	99	0	0	0	0·63	1·58	rev. red.[a]	13
II, posit. wave	0·1M t-Bu_4NClO_4	99	0	0	0	0·61	1·52	rev. red.	14
II, negat. wave	0·1M t-Bu_4NClO_4	0	2	99	0	1·05	2·62	radical dimerizat.	14
III, posit. wave	0·1M t-Bu_4NClO_4	0	12	99	0	1·23	3·08	radical dimerizat.[a]	13
III, negat. wave	0·1M t-Bu_4NClO_4	0	99	5	0	1·23	3·08	radical dimerizat.[a]	13
IV, posit. wave	0·1M t-Bu_4NClO_4	0	0	99	0	0·55	1·38	radical dimerizat.	13, 14
IV, negat. wave	0·1M t-Bu_4NClO_4	0	0	0	99	0·69	1·72	red. wave with prec. dimerizat.[a]	13

[a] Assumed mechanism. Depolarizers: *I* 4-(phenyl(methyl)methylene)-2,6-ditert-butyl-2,5-cyclohexadiene-1-one; *II* 4-(cyano(phenyl)methylene)-2,6-ditert-butyl-2,5-cyclohexadiene-1-one; *III* 4-benzylidene-2,6-ditert-butyl-2,5-cyclohexadiene-1-one; *IV* 4-cyanomethylene-2,6-ditert-butyl--2,5-cyclohexadiene-1-one.

of i_c and i_{lim}, comparable with experimental errors, are decisive for the diagnosis. This inaccuracy can be to some extent compensated for by choosing larger presumed errors in the mentioned quantities. An error in i_c and i_{lim} equal to the twenty-fold error in the instantaneous current was a satisfactory choice.

Under these conditions, values deviating from the theory as shown in Table I were obtained, although at the expense of a low selectivity among various functions. By repeating the calculation with more accurate values of i_c and i_{lim} for that type of function whose cost function was in the given set lowest, in combination with lowering the estimated error in i_c and i_{lim} to a value comparable with the error in the instantaneous current, a good discrimination can be attained. Moreover, by increasing the sampling density on the curve by a factor of 2–3 (points at 10–15 mV intervals), the selectivity increases by one or more orders of magnitude, however the calculations become time-consuming.

TABLE III

Influence of parameters of calculation on selectivity of statistical discrimination for the cathodic wave of 4-(phenyl(cyano)methylene)-2,6-ditert-butylcyclohexadiene-1-one. The instantaneous current in the first experimental point was 1 037·1 nA, in the last one 2 020·3 nA, their difference $i_{lim} = 983 \cdot 2$ nA

Function type	Estimated		Optimized		Cost function S/n	Acceptability, %
	i_c, nA	i_{lim}, nA	i_c, nA	i_{lim}, nA		
	1st approximation (11 points, $\sigma_c = \sigma_{lim} = 80$ nA, $\sigma_i = 5$ nA)					
1	1 022·1	1 028·2	1 045·85	941·95	0·7152	73
2	1 022·1	1 028·2	1 063·35	971·95	0·4464	94
3	1 022·1	1 028·2	1 052·10	978·20	0·3311	98
4	1 022·1	1 028·2	1 037·10	930·70	1·1133	35
	2nd approximation (11 points, $\sigma_c = \sigma_{lim} = 1 \cdot 49$ nA, $\sigma_i = 3 \cdot 72$ nA)					
1	1 052·1	978·2	1 052·10	978·20	1·4022	0
2	1 052·1	978·2	1 052·10	978·20	0·4495	48
3	1 052·1	978·2	1 052·10	978·20	0·1540	98
4	1 052·1	978·2	1 050·85	976·95	3·4254	0
	3rd approximation (30 points, $\sigma_c = \sigma_{lim} = 1 \cdot 00$ nA, $\sigma_i = 2 \cdot 50$ nA)					
1	1 052·1	978·2	1 050·85	978·20	1·3877	0
2	1 052·1	978·2	1 052·10	978·20	0·4419	1
3	1 052·1	978·2	1 052·10	978·20	0·1365	98
4	1 052·1	978·2	1 050·85	976·95	3·4541	0

The statistical discrimination of the curve types according to the given equations depends also on the preset error in the instantaneous current. If it is too large, all functions appear acceptable; if it is too small, it can happen that no one of the considered functions will be statistically acceptable. To obtain reliable results, the preset error in the instantaneous current must be close to the experimental error. The latter is, however, different in different cases and can be estimated only roughly.

The program enables one to calculate a simulated error in the instantaneous current, σ_i, so as to make the acceptability of a chosen function equal to a preset value (*e.g.*, 99% for the most probable function, or 1% for the least probable one). An absurd value of this error (too small or too large) indicates that the necessary assumptions for the analysis are not fulfilled. In the opposite case, if the acceptability of the other functions with a changed estimate of the error in the instantaneous current does not exceed 100% or drop below zero, the recalculated statistical analysis can be considered as significant.

Statistical evaluation of various combinations of simulated polarographic curves corresponding to known electrode processes (Table II) revealed that the mechanisms according to Eqs (*2*) and (*3*) are most difficult to distinguish from each other, since these processes with succeeding dimerization lead to very similar polarographic curves (Fig. 1).

The input data are almost without influence on the found value of $E_{1/2}$. However, when the calculation is carried out in a wider potential range, the found slope of the wave may be somewhat higher.

The application of the described method to polarographic curves of compounds with a known mechanism (Table II) led us to the same conclusions as in the case of simulated data. The influence of the discussed parameters on the selectivity of the statistical discrimination and on the course of iterations is given in Table III.

The statistical discrimination was further applied to a set of more than 150 quinomethide waves[13]; these could be attributed in all cases to one of the mentioned reaction types. Some typical examples are given in Table II.

The application of the described method to two or more-electron processes is (disregarding some exceptional cases) not physically justified. Calculations based on Eq. (*1*) can be, of course, used with advantage for the determination of the slope and $E_{1/2}$ value for any diffusion waves disregarding the number of transferred electrons or the degree of reversibility.

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Translated by K. Micka.