

# Automatic polarographic elucidation of electrode mechanisms by means of a knowledge-based system

## Part 1. Sampled d.c. polarography

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### ABSTRACT

A knowledge-based system has been developed for the automatic elucidation of electrochemical mechanisms. The system is based on sampled direct current (or Tast) polarography at a dropping mercury electrode as a technique for collecting experimental information and consists of a general expert system shell for the reasoning process, the specific set of rules and experimental modules. The set of rules allows the elucidation of eight relatively simple electrode reaction mechanisms fully automatically. The computer system has been validated with chemical systems the electrochemical behaviour of which is well established. All parts of the program are written in FORTH language for Apple II microcomputers. This expert system has an open character and new rules can be added to extend the set of mechanisms that can be determined.

Investigations of electrochemical reaction mechanisms are of importance for many branches of chemistry, especially in analytical chemistry, where the choice of a technique for the electrochemical determination of compounds of interest and the proper adjustment of the relevant variables is based on the mechanism of the reaction at the electrode. Recently, attention has been paid to the automation of the elucidation of these mechanisms, but this problem is hampered by the large number of simultaneous processes that can take place at the metal–solution interface and in its vicinity, e.g., multi-step electrochemical processes, adsorption, homogeneous reactions and equilibria involving electroactive species, electrocrystallization and layer formation. General strategies for the elucidation of mechanisms do not exist, so efficient mechanistic studies rely mostly on the experience and knowledge of the scientist. It is to be expected that in this situation the use of soft-

ware tools from the domain of artificial intelligence (knowledge-based or expert systems [1]) will be profitable. These systems use a human-like approach to problem solving: equipped with initial knowledge and rules of reasoning, they learn (extend the knowledge) from the results of activities and results of reasoning. Knowledge is collected until the problem can be solved, which means that the mechanism can be determined. Such systems have already been applied in several branches of analytical chemistry, especially spectroscopy [2–9] and chromatography [10–12]. A number of reviews on this topic have appeared recently [13–18].

In a previous paper [19], an expert system (CHROPO) using chronopotentiometry as the experimental technique was described. The program employed criteria collected by Reinmuth [20] and could be applied to only a limited number of mechanisms such as electron transfer reac-

tions and mechanisms in which electron transfer is coupled with subsequent chemical reactions (E and EC mechanisms, respectively). In this work, results of studies on electrode reaction mechanisms with the expert system using Tast polarography with a dropping mercury electrode (DME) are presented.

Sampled d.c. polarography was selected because several mechanisms, especially those in which an electroactive substance is produced in a preceding chemical step (CE mechanisms), could not be distinguished by chronopotentiometric measurements in the present version, some information can be obtained more easily from polarographic than from chronopotentiometric data and the dropping mercury electrode, the surface of which is regularly renewed, is much more useful in experiments with substances undergoing deposition on the electrode surface than a stationary mercury pool electrode. The development of this polarographic technique module to fit into the expert system was a new step in building a multi-technique system for electrochemical experiments. This complete system will eventually consist of complementary techniques to minimize the efforts needed to obtain particular information about a substance, and to compare results from different techniques in order to obtain a better decision

support. The proper operation of the program was checked using some well known standard electrochemical systems.

#### SOFTWARE

The program is capable of distinguishing eight relatively simple electrochemical mechanisms by testing the following parameters: slope of the logarithmic plot of  $\log[(i_L - i)/i]$  vs.  $E$ ; dependence of the half-wave potential,  $E_{1/2}$ , on the logarithm of the drop time; dependence of  $E_{1/2}$  on the logarithm of the concentration; dependence of the logarithm of the limiting current ( $i_L$ ) on the logarithm of the drop time ( $t_D$ ); dependence of  $i_L$  per unit concentration on the concentration itself. The list of mechanisms covered by this system is shown in Table 1 and the associated criteria are summarized in Table 2 (full equations on which criteria are based are given in the Appendix). Because criteria are valid only under certain restrictions (also presented in the Appendix), it is not possible to obtain the proper result when the mechanism studied is not well defined, or in the case of simultaneous, competitive mechanisms.

The whole program contains two different parts: the expert system shell and a set of experi-

TABLE 1  
Description of mechanisms that can be studied by the system

Symbol	Reaction	Description of the mechanism
$E$	$Ox \rightleftharpoons Red$	Fast heterogeneous electrode reaction (reversible electrochemical reaction)
$E_i$	$Ox \rightleftharpoons Red$	Slow electrode reaction (irreversible electrochemical reaction)
$E_a$	$Ox \leftrightarrow Ox^* \rightleftharpoons Red$	Fast electrode reaction from adsorbed state, fast adsorption equilibrium
$CE$	$A \rightleftharpoons Ox \rightleftharpoons Red$	Fast electrode reaction with preceding slow chemical reaction
$EC$	$Ox \rightleftharpoons Red \rightarrow A$	Fast electrode reaction with following irreversible chemical reaction
$EC_{dim}$	$Ox \rightleftharpoons Red$ $2Red \rightarrow A$	Fast electrode reaction with following irreversible product dimerization
$EC_{R,cat}$	$Ox \rightleftharpoons Red$ $Red + C \rightarrow Ox$	Fast electrode reaction with following fast catalytic regeneration
$EC_{R disp}$	$Ox \rightleftharpoons Red_1$ $2Red_1 \rightarrow Ox + Red_2$	Fast electrode reaction with following fast product disproportionation

TABLE 2

Criteria for the mechanisms

Criterion	Mechanism							
	$E$	$E_1$	$E_a$	$CE$	$EC$	$EC_{dim}$	$EC_{R,cat}$	$EC_{R,disp}$
$RT/slope \times nF$	1	$\neq 1$		$\neq 1$	1	$> 1$		
$(nF/RT)\delta E_{1/2}/\delta \ln t_D$	0	$\neq 0$			$\frac{1}{2}$	$\frac{1}{3}$		$\frac{1}{3}$
$(nF/RT)\delta E_{1/2}/\delta \ln C$	0	0			0	$\frac{1}{3}$		$\frac{1}{3}$
$\delta \log t_L/\delta \log t_D$	$\frac{1}{6}$	$\frac{1}{6}$	$-\frac{1}{3}$	$\frac{1}{6} a - \frac{2}{3}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6} a - \frac{2}{3}$	$\frac{7}{6}$
$\delta(t_L/C)/\delta C$	0	0	$< 0$	0	0	0	$< 0$	$> 0$

<sup>a</sup> Value 1/6 is excluded, i.e.  $\delta \log t_L/\delta \log t_D = 1/6$  test result must be false

mental modules. The expert system shell is a program performing the reasoning process, the knowledge management and the manipulation. It is essentially the same as that described in detail in the previous investigations [19]. The experimental part consists of three main blocks: a data acquisition block, a signal conditioning block and a data-handling block. In building this program, some ideas from Zollinger's program POLAR [21] were used. The whole program is written in FORTH language for Apple II computers.

#### Data acquisition block

This block contains routines for control of the potentiostat (via a D/A converter) and for data acquisition. The available potential range for the voltage scan is 2 V and the potential setting accuracy is 0.2 mV. Data in the Tast polarographic mode are collected during a 20-ms period starting 75 ms before the end of the drop life. Timing is based on the internal clock of the computer and by monitoring the hammer trigger output. The drop time can be varied from 0.4 to 4 s.

Each recorded polarogram is checked for artefacts. An indication of an artefact is based on the difference between raw and smoothed data; points for which this difference is greater than twice the mean difference for ten surrounding points are indicated as an artefact and then remeasured. Remeasurements are done until two subsequent new values do not differ significantly, and then the old value is replaced.

This procedure ensures that points which look like artefacts (polarographic maxima, high and narrow peaks, etc.) are retained, in contrast to

purely calculational refinement methods. The only restriction for the efficiency of this routine is that two artefacts should be separated by more than five data points.

#### Signal conditioning block

Routines from this block perform the 9-points wide quadratic Savitzky-Golay smoothing [22], followed by background subtraction of the previously recorded polarograms of the blank solution (edges of the polarogram are smoothed by series of the linear averaging filters of decreasing width). In the future, in this block the Fourier filter described by Aubanel et al. [23] will be used to perform filtering of very noisy or heavily artefacted (more than eight artefacts) polarograms.

#### Data handling block

In this block the recorded polarogram is analysed in order to extract information about the number and types of phenomena recorded (waves, peaks, maxima, etc.). Peaks are recognized by the examination of the first-derivative zero crossings, and waves by zero crossings of the second derivative. In derivative calculations, the Savitzky-Golay "smooth derivative" method [21] is employed; the first derivative is obtained using a 9-points wide second-order function, whereas the second derivative is calculated with both a 9- and a 17-points wide quadratic function. The 17-points wide function for the second derivative is more time consuming and is applied only to noisy polarograms, for which a narrower function does not yield good results.

The wave parameters (half-wave potential, limiting current and slope of wave) are obtained from three-parameters least-squares curve-fitting [24]. In this fitting procedure, all points of the wave for which the current was greater than 10% and less than 90% of the estimated limiting current are used. An initial estimate of the half-wave potential is calculated from the second-derivative zero crossing, and the slope of the wave is estimated from Tomes's criterion [25] of  $E_{3/4} - E_{1/4}$  difference. Curve fitting is performed until the estimated corrections do not exceed 0.1 mV for  $E_{1/2}$ , 0.1% for the limiting current and 0.1 mV/ln  $t$  for the wave slope. The decisions in the expert system are made on a statistical basis. Therefore, a statistical test (Student's  $t$ -test) is included in this block.

## EXPERIMENTAL

The validation of the program was done with the following compounds and systems, for which the reduction mechanisms are well defined:  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ , formaldehyde in water, cinnamaldehyde at

pH 1 and iron(III)-oxalate complex in presence of hydrogen peroxide. The experimental set-up consisted of a Basis-108 microcomputer (Apple II + compatible), equipped with a Digilog 12-bit A/D converter and a Kronemuis 12-bit D/A converter, an E 506 Polarecord (Metrohm) polarographic analyser used as a potentiostat and a E 505 polarographic stand.

Cadmium chloride and potassium chloride were Suprapur products and all other reagents were of analytical-reagent grade. Water was provided by a Millipore Q-II system. Oxygen was expelled by bubbling specially pure nitrogen (Hoekloos) through the solution.

## RESULTS AND DISCUSSION

The program performed both the experimental measurements and reasoning properly. For the reduction of cadmium in potassium chloride medium the simple reversible mechanism ( $E$ ) was established (Table 3) and for chromium in sodium perchlorate solution (Table 4) simple reaction rate-controlled mechanism ( $E_1$ ) was found. The

TABLE 3

Investigation of Cd(II) reduction mechanism

(Supporting electrolyte 1.0 mol dm<sup>-3</sup> KCl Concentration varied in the range  $4.9 \times 10^{-5}$ – $3.8 \times 10^{-4}$  mol dm<sup>-3</sup>, drop time varied in the range 400–4000 ms)

Hypothesis tested	Confidence range of the numerical argument	Conclusion(s), decision(s)
$\delta(t_L/C)/\delta C = 0$	-1 84247-0 18671 <sup>a</sup>	$\delta(t_L/C)/\delta C = 0$ is true Mechanism = $EC_{R,cat}$ is false
$\delta \log t_L/\delta \log t_D = 1/6$	0 16198-0 18771	$\delta \log t_L/\delta \log t_D = 1/6$ is true Mechanism = $CE$ is false
$(\delta E_{1/2}/\delta \ln t_D)nF/RT = 0$	-0 11887-0 10896	$(\delta E_{1/2}/\delta \ln t_D)nF/RT = 0$ is true Mechanism = $E_1$ is false
$(\delta E_{1/2}/\delta \ln C)nF/RT = 0$ $RT/\text{slope} \times nF = 1$	-0 00121-0 00374 0 77605-1 15305	$(\delta E_{1/2}/\delta \ln C)nF/RT = 0$ is true $RT/\text{slope} \times nF = 1$ is true Mechanism = $E$ is true Mechanism = $EC_{dim}$ is false
$\delta \log t_L/\delta \log t_D = -1/3$	0 16198-0 18771	$\delta \log t_L/\delta \log t_D = -1/3$ is false Mechanism = $E_a$ is false
$(\delta E_{1/2}/\delta \ln t_D)nF/RT = 1/2$	-0 11887-0 10896	$(\delta E_{1/2}/\delta \ln t_D)nF/RT = 1/2$ is false Mechanism = $EC$ is false
$\delta \log t_L/\delta \log t_D = 7/6$	0 16198-0 18771	$\delta \log t_L/\delta \log t_D = 7/6$ is false Mechanism = $EC_{R,disp}$ is false

<sup>a</sup> Arbitrary units

TABLE 4

## Investigation of Cr(III) reduction mechanism

(Supporting electrolyte: 1.0 mol dm<sup>-3</sup> NaClO<sub>4</sub> Concentration varied in the range 2.0 × 10<sup>-4</sup>–1.25 × 10<sup>-3</sup> mol dm<sup>-3</sup>, drop time varied in the range 400–1400 ms)

Hypothesis tested	Confidence range of the numerical argument	Conclusion(s), decision(s)
$\delta(t_L/C)/\delta C = 0$	-8 171796–0 02932 <sup>a</sup>	$\delta(t_L/C)/\delta C = 0$ is true Mechanism = $EC_{R,cat}$ is false
$\delta \log t_L/\delta \log t_D = 1/6$	0 12869 -0 21930	$\delta \log t_L/\delta \log t_D = 1/6$ is true Mechanism = $CE$ is false
$(\delta E_{1/2}/\delta \ln C)nF/RT = 0$	-0 013918–0 64539	$(\delta E_{1/2}/\delta \ln C)nF/RT = 0$ is true
$(\delta E_{1/2}/\delta \ln t_D)nF/RT = 0$	0 83151 -1 21631	$(\delta E_{1/2}/\delta \ln t_D)nF/RT = 0$ is false Mechanism = $E$ is false
$RT/\text{slope} \times nF = 1$	0 42148 -0 82148	$RT/\text{slope} \times nF = 1$ is false Mechanism = $E_1$ is true Mechanism = $EC$ is false
$\delta \log t_L/\delta \log t_D = -1/3$	0 12869 -0 21930	$\delta \log t_L/\delta \log t_D = -1/3$ is false Mechanism = $E_a$ is false
$(\delta E_{1/2}/\delta \ln C)nF/RT = 1/3$	-0 013918–0.64539	$(\delta E_{1/2}/\delta \ln C)nF/RT = 1/3$ is true
$(\delta E_{1/2}/\delta \ln t_D)nF/RT = 1/3$	0 83151 -1 21631	$(\delta E_{1/2}/\delta \ln t_D)nF/RT = 1/3$ is false Mechanism = $EC_{dim}$ is false
$\delta \log t_L/\delta \log t_D = 7/6$	0 12869 -0 21930	$\delta \log t_L/\delta \log t_D = 7/6$ is false Mechanism = $EC_{R,disp}$ is false

<sup>a</sup> Arbitrary units

result of the study of formaldehyde reduction in water indicated a  $CE$  mechanism (Table 5) whereas in the case of Fe(III/II)–oxalate system

in presence of hydrogen peroxide (Table 6) the regenerative catalytic mechanism ( $EC_{R,cat}$ ) was established. Experiments with cinnamaldehyde re-

TABLE 5

## Investigation of formaldehyde reduction mechanism in water

(Supporting electrolyte 0.9 mol dm<sup>-3</sup> KCl, pH = 11.0 Concentration varied in the range 0.0100–0.0225 mol dm<sup>-3</sup>, drop time varied in the range 400–1000 ms)

Hypothesis tested	Confidence range of the numerical argument	Conclusion(s), decision(s)
$\delta(t_L/C)/\delta C = 0$	-8 51994–8 44593 <sup>a</sup>	$\delta(t_L/C)/\delta C = 0$ true Mechanism = $EC_{R,cat}$ is false
$\delta \log t_L/\delta \log t_D = 1/6$	0 17635–0.68843	$\delta \log t_L/\delta \log t_D = 1/6$ is false Mechanism = $E$ is false Mechanism = $E_1$ is false Mechanism = $EC$ is false Mechanism = $EC_{dim}$ is false
$\delta \log t_L/\delta \log t_D = -1/3$	See above	$\delta \log t_L/\delta \log t_D = -1/3$ is false Mechanism = $E_a$ is false
$\delta \log t_L/\delta \log t_D > 1/6$	See above	$\delta \log t_L/\delta \log t_D > 1/6$ is true
$\delta \log t_L/\delta \log t_D < 2/3$	See above	$\delta \log t_L/\delta \log t_D < 2/3$ is true
$RT/\text{slope} \times nF = 1$	0 62978–0 63525	$RT/\text{slope} \times nF = 1$ is false Mechanism = $CE$ is true
$\delta(t_L/C)/\delta C > 0$	8 51994–8 44593 <sup>a</sup>	$\delta(t_L/C)/\delta C > 0$ is true
$\delta \log t_L/\delta \log t_D = 7/6$	0.17636–0 68843	$\delta \log t_L/\delta \log t_D = 7/6$ is false Mechanism = $EC_{R,disp}$ is false

<sup>a</sup> Arbitrary units

TABLE 6

Investigation of the reduction mechanism of the Fe(III)–oxalate complex in the presence of hydrogen peroxide (Supporting electrolyte:  $0.18 \text{ mol dm}^{-3} \text{ H}_2\text{C}_2\text{O}_4\text{--Na}_2\text{C}_2\text{O}_4 + 1.19 \times 10^{-2} \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$  (pH = 3.5). Concentration varied in the range  $1.2 \times 10^{-4}\text{--}4.0 \times 10^{-4} \text{ mol dm}^{-3}$ , drop time varied in the range 400–2000 ms)

Hypothesis tested	Confidence range of the numerical argument	Conclusion(s), decision(s)
$\delta(t_L/C)/\delta C = 0$	$-1.93465\text{--}0.527944^a$	$\delta(t_L/C)/\delta C = 0$ is false Mechanism = $E$ is false Mechanism = $E_1$ is false Mechanism = $CE$ is false Mechanism = $EC$ is false Mechanism = $EC_{\text{dim}}$ is false
$\delta(t_L/C)/\delta C < 0$	See above	$\delta(t_L/C)/\delta C < 0$ is true
$\delta \log t_L/\delta \log t_D = -1/3$	$0.20278\text{--}0.33077$	$\delta \log t_L/\delta \log t_D = -1/3$ is false Mechanism = $E_a$ is false
$\delta \log t_L/\delta \log t_D > 1/6$	See above	$\delta \log t_L/\delta \log t_D > 1/6$ is true
$\delta \log t_L/\delta \log t_D < 2/3$	See above	$\delta \log t_L/\delta \log t_D < 2/3$ is true Mechanism = $EC_{\text{R,cat}}$ is true
$\delta \log t_L/\delta \log t_D = 7/6$	See above	$\delta \log t_L/\delta \log t_D = 7/6$ is false Mechanism = $EC_{\text{R,disp}}$ is false

<sup>a</sup> Arbitrary units

sulted in a decision that the electron transfer step is followed by a dimerization ( $EC_{\text{dim}}$  mechanism) (Table 7).

Based on the experiments, it can be stated that

the program is capable of recognizing the mechanism considered in a relatively short time. In the configuration used, one complete elucidation takes about 8 h. About 40% of the total run time is

TABLE 7

Investigations of reduction mechanism of cinnamaldehyde

(Supporting electrolyte  $0.1 \text{ mol dm}^{-3}$  glycine/HCl buffer–ethanol (70/30), pH = 1.0. Concentration varied in the range  $2.0 \times 10^{-5}\text{--}1.6 \times 10^{-4} \text{ mol dm}^{-3}$ , drop time varied in the range 400–2000 ms)

Hypothesis	Confidence range of the numerical argument	Conclusion(s), decision(s)
$\delta(t_L/C)/\delta C = 0$	$-8.3360\text{--}1.07867^a$	$\delta(t_L/C)/\delta C = 0$ is true Mechanism = $EC_{\text{R,cat}}$ is false
$\delta \log t_L/\delta \log t_D = 1/6$	$0.14237\text{--}0.27343$	$\delta \log t_L/\delta \log t_D = 1/6$ is true Mechanism = $CE$ is false
$(\delta E_{1/2}/\delta \ln C)nF/RT = 0$	$0.31162\text{--}0.67732$	$(\delta E_{1/2}/\delta \ln C)nF/RT = 0$ is false Mechanism = $E$ is false Mechanism = $E_1$ is false Mechanism = $EC$ is false
$\delta(t_L/C)/\delta C < 0$	$-8.3360\text{--}1.07867^a$	$\delta(t_L/C)/\delta C < 0$ is true
$\delta \log t_L/\delta \log t_D = -1/3$	$0.14237\text{--}0.27343$	$\delta \log t_L/\delta \log t_D = -1/3$ is false Mechanism = $E_a$ is false
$(\delta E_{1/2}/\delta \ln C)nF/RT = 1/3$	$0.31162\text{--}0.67732$	$(\delta E_{1/2}/\delta \ln C)nF/RT = 1/3$ is true
$(\delta E_{1/2}/\delta \ln t_D)nF/RT = 1/3$	$0.17148\text{--}0.47645$	$(\delta E_{1/2}/\delta \ln t_D)nF/RT = 1/3$ is true
$RT/\text{slope} \times nF = 1$	$1.06124\text{--}1.61962$	$RT/\text{slope} \times nF = 1$ is false Mechanism = $EC_{\text{dim}}$ is true
$\delta \log t_L/\delta \log t_D = 7/6$	$0.14237\text{--}0.27343$	$\delta \log t_L/\delta \log t_D = 7/6$ is false Mechanism = $EC_{\text{R,disp}}$ is false

<sup>a</sup> Arbitrary units

spent on experiments and another 40% on curve fitting, which is the most time-consuming procedure. The remaining 20% is used for the reasoning process, for other calculations, for input/output operations and for management of the overlay structure of the program.

In the present version, the program can be used for the fully automated elucidation of simple electrochemical mechanisms. The contribution of the operator is limited to the actions dealing with the experimental hardware which cannot be executed by the computer (e.g., change of the drop time with the E 506 polarograph). The number of mechanisms covered by the set of rules will be extended. Work is also in progress to increase the number of different electrochemical techniques.

## APPENDIX

For all mechanisms simplifying assumptions were made, namely that all electrochemical processes proceed under linear diffusion conditions and equality of diffusion coefficients of the reduced and oxidized forms of the substances is assumed. A survey of the equations that form the basis of the mechanism criteria is presented below [26,27].

### *E mechanism (fast electron transfer reaction)*

The Ilkovic equation:

$$i_L = \text{constant} \times n c_{\text{ox}} D_{\text{ox}}^{1/2} m^{2/3} t^{1/6}$$

forms the basis for the criteria  $\delta(i_L/C_{\text{ox}})/\delta C_{\text{ox}} = 0$  and  $\delta \log i_L / \delta \log t_D = 1/6$ . The wave equation

$$E = E^0 + \text{constant} + (RT/nF) \ln[(i_L - i)/i]$$

where the constant is a term depending on activity coefficients, leads to the criteria  $\delta E_{1/2} / \delta \ln C_{\text{ox}} = 0$  and  $\delta E_{1/2} / \delta \ln t_D = 0$ . The slope of the wave is  $RT/nF$ , so the parameter  $RT/\text{slope} \times nF$  should be equal to 1 when this mechanism is applicable.

### *E<sub>i</sub> mechanism*

In the potential region corresponding to the wave plateau, the current is diffusion-controlled and described by the Ilkovic equation, so the criteria involving  $\delta(i_L/C_{\text{ox}})/\delta C_{\text{ox}}$  and  $\delta \log i_L /$

$\delta \log t_D$  are identical with the reversible case. The half-wave potential can be described (assuming that the electron-transfer coefficient  $\alpha$  is independent of potential) by the equation [28]

$$E_{1/2} = E^0 + (RT/\alpha nF) \times \ln(\text{constant} \times k_{\text{fh}}^{\circ} t^{1/2} / D_{\text{ox}}^{1/2})$$

where the value of the constant depends also on the units in which variables in the logarithmic term are expressed, and  $k_{\text{fh}}$  is a heterogeneous reaction rate constant. On the basis of this equation, the criteria  $\delta E_{1/2} / \delta \ln t_D \neq 0$ ,  $\delta E_{1/2} / \delta \ln C_{\text{ox}} = 0$  and  $RT/\text{slope} \times nF \neq 1$  can be easily obtained.

### *E<sub>a</sub> mechanism*

Based on Brdicka's theory [29], adsorption of the substrate or product of an electrode reaction leads to post- or pre-wave formation, respectively. The pre- or post-wave grows with an increase in concentration until it reaches a limiting value corresponding to complete surface coverage. Hence  $\delta(i_L/C_{\text{ox}})/\delta C_{\text{ox}} < 0$  holds for the adsorptive wave. The current can be described by the equation [29]

$$i_L^{\text{ads}} = \text{constant} \times n F m^{2/3} t^{-1/3}$$

where the constant is related to the concentration of the adsorbed form, the adsorption equilibrium constant and the maximum coverage factor. From this equation, the dependence of the limiting current on the drop time is  $\delta \log i_L / \delta \log t_D = -1/3$ .

### *CE mechanism*

Criteria for the CE mechanism are based on Koutecky's solution [30], under the assumption that the equilibrium constant of the preceding chemical reaction is  $K \ll 1$ . The current can be described by the function

$$i_L = i_d F(\chi)$$

where

$$\chi = \sqrt{12t/7D} (k_{\text{fh}} + k_{\text{bh}})$$

and  $i_d$  is a current which would flow under diffusion-controlled conditions. The function  $F$  can be

expressed approximately in the form

$$F(\chi) = \text{constant}_1 \sqrt{Kk_1 t} / (1 + \text{constant}_2 \sqrt{Kk_1 t})$$

Thus, for various values of  $Kk_1 t$ ,  $\delta \log i_L / \delta \log t_D$  varies from 1/6 (for  $Kk_1 t \Rightarrow \infty$ ) to 2/3 (for  $Kk_1 t \Rightarrow 0$ ); nevertheless, when it is equal to 1/6, the  $E_i$  and  $CE$  mechanisms are not distinguishable. The value of  $\delta(i_L/C_{ox})/\delta C_{ox}$  is 0. Because the Nernst equation does not hold at the surface,  $RT/\text{slope} \times nF < 1$ .

#### *EC mechanism*

Under the assumption that the rate constant  $k_1$  has a moderate value, the equation of the polarographic wave for a first-order following chemical reaction can be written in the form [31]

$$E = E^0 + (RT/nF) \ln[(i_L - i)/i] \\ + \text{constant} + (RT/2nF) \ln(k_1 t)$$

and from this equation the criteria  $RT/\text{slope} \times nF = 1$ ,  $\delta E_{1/2}/\delta \ln t_D = RT/2nF$  and  $\delta E_{1/2}/\delta \ln C_{ox}$  can be easily calculated. Because the current is limited by diffusion,  $\delta \log i_L / \delta \log t_D = 1/6$  and  $\delta(i_L/C_{ox})/\delta C_{ox} = 0$ .

#### *EC<sub>dim</sub> mechanism*

Assumption of an  $E$  step leads automatically to the criteria  $\delta \log i_L / \delta \log t_D = 1/6$  and  $\delta(i_L/C_{ox})/\delta C_{ox} = 0$ . With an extra assumption that dimerization is fast and irreversible, the half-wave potential is equal to [32]

$$E_{1/2} = E^0 - (RT/nF) \text{constant} \\ + (RT/3nF) \ln(C_{ox} k_1 t)$$

and the criteria are  $\delta E_{1/2}/\delta \ln t_D = RT/3nF$  and  $\delta E_{1/2}/\delta \ln C_{ox} = RT/3nF$ .

#### *EC<sub>R,cat</sub> mechanism*

According to Koutecky [33], the limiting current in such a reaction (pseudo-first-order) mechanism is equal to

$$i_L/i_d = \psi(\gamma)$$

where  $\gamma = k_1 C_c t$  and, as before,  $i_L$  is the recorded limiting current and  $i_d$  is a current which would flow under conditions of pure diffusion control.

Using limiting values for the function  $\psi$ :

$$\gamma \rightarrow 0 \Rightarrow \psi(\gamma) \rightarrow 1$$

$$\gamma \rightarrow \infty \Rightarrow \psi(\gamma) \rightarrow \text{constant} \times \gamma^{1/2}$$

it can be stated that the value of  $\delta \log i_L / \delta \log t_D$  varies from 1/6 to 2/3 when  $\delta(i_L/C_{ox})/\delta C_{ox} = 0$ . When the assumption of constancy of  $C_c$  is rejected,  $\delta(i_L/C_{ox})/\delta C_{ox}$  becomes less than zero, which is implemented as a condition in the present program and means that also second-order  $EC_{R,cat}$  processes can be studied.

#### *EC<sub>R,disp</sub> mechanism*

According to Koutecky and Koryta [34], with a later extension by Kastening [35], the ratio of the recorded limiting current to the theoretical diffusion-controlled limiting current can be expressed in the form of a series:

$$i_L/i_d = 1 + \sum_{i=1}^{\infty} L_i (2C_{ox} k_1 t)^i$$

and the criteria are  $\delta(i_L/C_{ox})/\delta C_{ox} > 0$  and  $\delta \log i_L / \delta \log t_D > 1$  when the value of  $C_{ox} k_1 t_D$  is large enough. Values of  $\delta E_{1/2}/\delta \ln t_D$  and  $\delta E_{1/2}/\delta \ln C_c$  are both equal to  $RT/3nF$  [27].

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