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THE USE OF POLAROGRAPHY IN THE INITIAL STAGES OF INVESTIGATIONS OF MECHANISMS OF ORGANIC ELECTRODE PROCESSES IN AQUEOUS SOLUTIONS[1]

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Initial procedure used in investigation of an organic compound that has not been studied by polarography is described. This is followed by determination of the number of transferred electrons, elucidation of the nature of the process controlling the limiting current, discussion of the role of acid-base equilibria, and proofs of reversibility of the electrode process. Numerous examples demonstrating the use of experimental data in elucidation of the sequence of electron and proton transfers in electroorganic processes in protic solvents are given.

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[1] Based on a lecture given on April 28,1998 at the Department of Analytical Chemistry of the Faculty of Chemical Technology at Pardubice

Introduction

For application of any analytical procedure — whether gravimetric, volumetric, spectrophotometric, chromatographic or electrochemical — it is essential to understand at least the main features of physical and chemical processes involved. Only with such understanding it is possible to find rationally the optimum reaction conditions and in many cases either to predict or to interpret matrix effects. The physical quantity measured is usually straightforward — the mass, the volume, the absorbance or reflectance, the conductance, the potential, or the current and these quantities are measured either at equilibrium or under conditions where the rate of the reaction plays important role.

The chemical aspect involves known composition of the product which has a well defined property, such as limited solubility, limited dissociation or complex formation, absorptivity, or fluorescence, molar conductivity, or standard oxidation-reduction potential, or an interaction with a substrate, as in chromatography. The situation is more complicated in dynamic electrochemical techniques, such as polarography (where current-voltage curves are obtained with a dropping mercury electrode) and voltammetry (where such curves are obtained with electrodes the surface of which is not renewed). In the latter cases, in addition to the thermodynamic standard potential also the rates of electron transfer as well as rates and equilibria of chemical reactions, which can take place before the first electron uptake, between two electron uptakes, as well as after some electron uptakes can play a role. Moreover, as such electrochemical processes take place at the interface between a metallic phase and a solution, adsorption of studied compound at the electrode surface can play a role.

The ultimate goal of any electrochemical study is to understand the nature of the electron transfer and chemical reactions and to determine all equilibrium and rate constants involved, as well as to evaluate quantitatively the role of adsorption on these processes. To achieve such goal involves extensive, long term studies using numerous techniques. More or less complete understanding on this level has been so far achieved for a relatively few systems and is not a condition for practical application of electroanalytical procedures. For such applications is nevertheless essential to recognize the number of electrochemical steps, the numbers of electrons transferred in each of those steps, the nature of chemical reactions accompanying each individual electron transfer, and to obtain some information about position of equilibria and rates of chemical reactions involved. A general piece of information about how much and how adsorption affects the processes studied is useful. Usually, both for mechanistic and analytical applications conditions are sought under which the role of adsorption is minimal (with the exception of adsorption stripping analyses).

For inorganic species the recognition of the relevant physical and chemical steps is often fairly straightforward (with the exception of inorganic electroactive centers placed inside large — e.g. protein-molecules). For substitution inert complexes the structure of the electroactive species is known. It is necessary to distinguish whether the central metal or the ligand or both undergo electron transfer reactions and for the metal to establish the change in the oxidation state (for electroactive organic ligands the behavior of the ligand must be investigated first). For labile complexes the composition of the complex or complexes formed and its stability should be known in addition to the change in oxidation states. The nature of aquocomplexes or of complexes formed in a given supporting electrolyte in the absence of investigated ligand plays sometimes also an important role.

For organic compounds the situation is different, depending on whether aprotic or protic solvents are used. In aprotic solvents the first electron uptake is usually not preceded by a chemical reaction, such as proton transfer. The use of such solvents enables us thus a more straightforward information about the thermodynamics of the first electron transfer. On the other hand, the radical ions, anions or cations, formed in the electron uptake, are strong acids or bases and readily undergo reactions with any proton sources or bases present, such as solvent molecules, components of supporting electrolytes or parent compounds. As systems are not buffered in such components, higher order reactions, which are more difficult to follow, are often involved. Addition of reactants particularly reactive towards the products of electrolysis are sometimes useful, particularly in synthetic application.

Most analytical applications of polarographic and voltammetric determination of organic compounds are carried out in aqueous solutions. Hence this contribution will be restricted to such systems.

The surface of solid electrodes is generally much less well defined than that of mercury. This and a more pronounced role of adsorption on solid electrodes makes them less suitable for gathering initial information. Furthermore, this author is much less familiar with organic electrode processes on solid electrodes. Thus this contribution will be restricted to processes occurring at mercury electrodes. This presents a serious limitation: Since mercury is dissolved in aqueous solutions at about +0.4 V (SCE), the behavior of less easily electrooxidized species cannot be discussed here.

One comment should be made concerning the use of mercury electrodes: In some countries, e.g. Scandinavian, the use of metallic mercury in chemical laboratories is practically prohibited.

As metallic mercury, even when spilt at room temperature, results in vapor pressure orders of magnitude below the toxic level, such prohibition is a hysterical overreaction without scientific foundation. The present author over past 50 years not only worked in laboratories where mercury was daily used, but met hundreds of colleagues who did so without any harmful effects. Only at elevated temperatures, e.g. where distilled, metallic mercury is toxic.

A situation of development of an analytical method for an organic compound in aqueous solutions which has not been studied before is not unusual. Among the four million or so of known organic compounds at least 50% can be expected to be electroactive, i.e. to undergo either electrooxidation or electroreduction. Out of the two million compounds considerably less than 100,000 have been studied using electrochemical method and less than 10,000 studied in some detail. There are whole classes of compounds, in particular among heterocyclic compounds, which have not been studied before.

Thus when facing the problem of investigation of an unstudied compound, it is first useful to check, whether the compound contains a grouping which is known to be electroactive at mercury electrodes.

Most important reducible groups are the following

$C-F^*$ $C-Cl^*$ $C-Br$ $C-I$ $C-NR-^*$ $C-SR^*$ $C-OR^*$

$C=C^*$ $C=O$ $C=N$ $C=S$

$C\equiv C^*$ $C\equiv N^*$

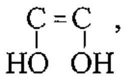
$N-N^*$ $N=N$ $N\equiv N$

$N=O$ NO_2

$O-O$ $S-S$

Polycondensed aromatics, some heterocyclics, quinones and their nitrogen analoga.

Most important groupings which undergo oxidations at mercury electrodes



$\underset{HO}{C}=\underset{OH}{C}$, CHO, NHOH*, —HNNH—*, hydroquinones and their nitrogen analoga

Groups marked with an asterisk above undergo reduction or oxidation within the potential range available in aqueous solutions only when they form a part of a conjugated system or in the presence of another activating grouping in the molecule. For example, the single C–N bond is not reduced in aliphatic amines, but is reducible in α-aminoketones or in 4-pyridylmethylamine.

Anodic waves can be observed also in the presence of organic compounds which form slightly soluble or complex compounds with mercury, for example thiols, derivatives of urea and thiourea and some heterocyclic compounds.

If the studied compound contains a known electroactive center, it is necessary to check in the literature if it behaves like some earlier described system. In such case it is sufficient to prove that the investigated compound shows the same number of waves, the same number of electrons transferred in each of them and a similar dependence of limiting currents and half-wave potentials on pH, and/or ionic strength, solvent composition and concentration, as related compounds described in the literature.

Initial Experiments

When, on the other hand, the studied compound shows a behavior different from that of related compounds described in literature or if this compound does not contain a known reactive center, a systematic procedure should be carried out. One approach to such study, which has proved useful in numerous cases, can be described as follows

1) Prepare a 0.01 M stock solution of the studied compound either in water, or in an organic solvent miscible with water, such as ethanol, acetonitrile, DMF, DMSO or tetrahydrofuran. Verify that the compound is completely dissolved in true — not colloidal — solution. Check the stability of the stock solution by recording current-voltage curves over chosen time intervals. According to results of such study prepare stock solution every week, every day or every hour (possibly keeping it at low temperature).
2) Prepare the following set of supporting electrolytes

0.1 M H_2SO_4	pH ≈ 1
0.1 M acetate buffer	pH 4.7
0.05 M phosphate buffer	pH 6.8
0.05 M borax	pH 9.3
0.1 M NaOH	pH ≈ 13

Deaerate each supporting electrolyte by a stream of inert gas (N_2, Ar), add an aliquot of the stock solution so that final concentration in the electrolytic cell is 0.1 mM, introduce briefly inert gas and record a current-voltage curve using dc polarography. For 0.1 M H_2SO_4 and 0.1 M NaOH it is recommended to record two current-voltage curves in succession: Any observed changes would indicate an acid or base catalyzed cleavage.

3) Observe in which pH the compound is electroactive, i.e. gives either a cathodic wave (indicating a reduction) or an anodic one (indicating either an oxidation or formation of a mercury compound).

Next it is to be noted, if at each pH a single or a multiple wave is observed. Does in the case of multiple waves their ratio change with pH? At all pH-values where a wave is observed but particularly at those pH-values where multiple waves are observed, vary concentration of the studied compound at least over one order of magnitude — for example between 0.05 mM and 0.5 mM. Are all waves a linear function of concentration? If multiple waves are observed, does the ratio of limiting currents change with concentration of the electroactive species?

The majority of limiting currents encountered in polarography are controlled by diffusion and such currents are a linear function of concentration of the electroactive species (Fig. 1a). Nevertheless, also currents governed by a rate of a first order chemical reaction (kinetic waves) and some catalytic waves can also show a linear dependence on concentration. A current which increases linearly with increasing concentration of the electroactive species, but becomes independent of concentration above a certain concentration, is an adsorption current, which involves rapid formation of an adsorbate (Fig. 1b). Gradual increase in current reaching a limiting value (Fig. 1c) was observed for some types of adsorption currents (with a more sluggish formation of the adsorbed layer) and some catalytic currents.

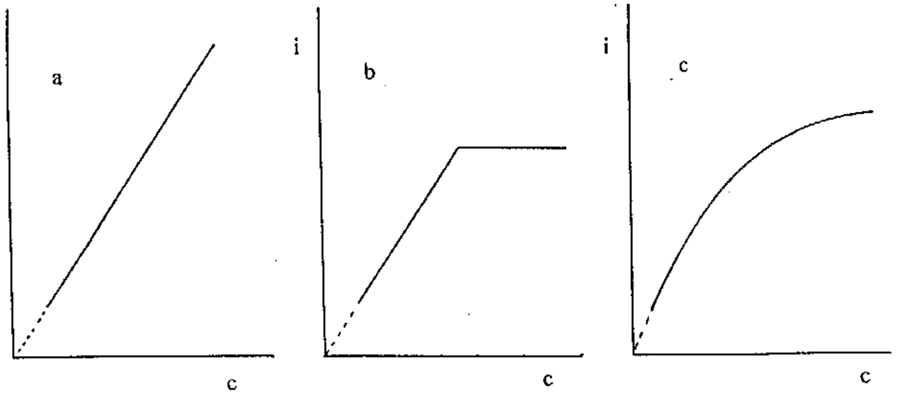


Fig. 1 Dependence of the limiting current on concentration of the electroactive species: (a) Diffusion, kinetic and some catalytic currents; (b) adsorption currents, fast formation of adsorbate; (c) adsorption currents, slow formation of adsorbate, some catalytic currents

It is strongly recommended to use dc polarography with a natural dropping electrode for such studies. Limiting currents are not affected by the rates of electrode processes, whereas peak currents as measured in differential pulse polarography or linear sweep or cyclic voltammetry depend also on kinetics of the electrode process. Also the use of tast (sampled) polarography and the use of static mercury drop and similar types of electrodes is less advantageous, as for such conditions the current characteristics in the presence of adsorption or antecedent chemical reactions are less well understood.

Determination of Number of Electrons

Perhaps the most important piece of information about any electrochemical process is the number of electrons transferred in a given step of the reduction or oxidation process.

The simplest and at the same time most informative approach is comparison of limiting currents of the studied compound with limiting currents of equimolar solutions of standards — either external or internal. For external standards are used well defined compounds (98% or better purity; when crystal water is present, it should be well defined) of similar size of molecules and with known number of electrons transferred in the reduction or oxidation. These waves are usually recorded in the same supporting electrolyte as the wave of the studied solution. Typical examples involve quinones ($n = 2$; well soluble quinones bearing OH or SO_3^- groups are particularly suitable), aryl alkyl or diaryl ketones ($n = 1$ in acidic and alkaline solutions, $n = 2$ in the medium pH-range), azo compounds ($n = 2$, with exception of *o*- and *p*-hydroxy and -amino derivatives), nitrobenzenes ($n = 4$ with exception of *o*- and *p*-hydroxy and amino derivatives), semicarbazones or oximes ($n = 4$ at sufficiently low pH-values).

The limiting currents of the investigated compound and standards (preferably 2 – 3) are compared and observed if they are equal, a fraction (e.g. one half) or a multiple (e.g. twice as high) (Fig. 2a). For molecules of comparable molecular mass the differences in diffusion coefficients (which in the expression for current are in square root) are negligible for estimation or unit values of "*n*". This technique is of course unsuitable when small deviations from unit values of "*n*" are of interest, but this is not the case in the initial stages of investigation. Peak currents, as obtained by differential pulse polarography, linear sweep or cyclic voltammetry are not suitable for this procedure, as these currents depend also on kinetic parameters of electrode processes.

Sometimes the studied molecule contains in addition to the investigate grouping another electroactive group, for which the "*n*" is known. Comparison of the ratio of the limiting currents for the unknown with those of the internal standard yields the value of "*n*" (Fig. 2b).

Coulometry is often applied to the determination of "*n*", but certain *caveats* must be considered when used for elucidation of processes at the dropping mercury electrode. Chemical and electrochemical processes which take place during the approximately 3 second of the life of a single drop can be different from those, occurring over longer periods of time needed for controlled potential electrolysis used in coulometry. And if — as most frequently done — a constant surface electrode, such as mercury pool, is used, — differences may result not only from consecutive bulk reactions but also from adsorption at the electrode surface and reactions in the adsorbed state. Therefore ,it is important to compare for the studied compound the current-voltage curves obtained with the use of dropping mercury

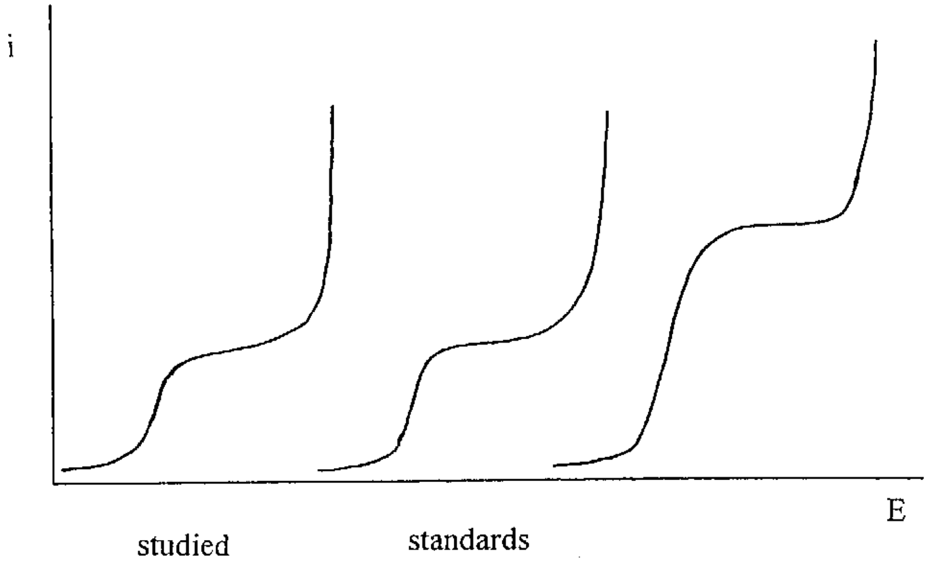


Fig. 2a Determination of the number of transferred electrons by comparison of limiting currents: First curve – studied compound, second and third – standards. Equimolar concentrations

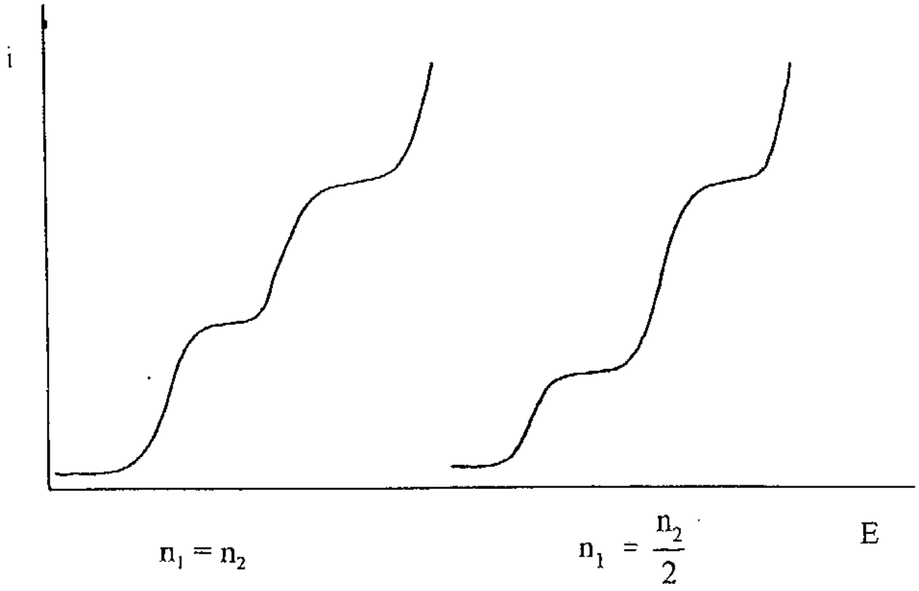


Fig. 2b Determination of the number of transferred electrons using internal standard from ratio of limiting currents of two electroactive groups, when n_1 or n_2 is known

electrode (DME), hanging mercury drop electrode (HMDE) and mercury pool (Hg-pool) electrode. If all these three curves show similarities, it is safe to use HMDE or Hg-pool as the working electrode. When Hg-pool is used, a current-voltage curve *with this electrode* should always be recorded (usually point by point). The choice of the potential of the Hg-pool should be based on such i-E curve, not on the curve obtained by DME. The surface of the Hg-pool should be equipotential, which can be achieved by a proper positioning of the counter electrode.

When the potential for the controlled potential electrolysis has been properly chosen (so that the role of consecutive electrochemical processes is minimized, often close to the upper bend of the current-voltage curve, before the limiting current is reached), first it is found out whether the rate of electrolysis follows first order kinetics. Deviations from linear $\ln i = f(t)$ [or $\ln c = f(t)$] plot indicate complications, e.g. due to consecutive chemical reactions of the primary product.

To determine the value of "n" it is possible to compare the slope of the $i = f(t)$ plot with a slope obtained for controlled potential electrolysis with a compound with known "n", such as quinones, Cd^{2+}, or Ti^{+} ions. Alternatively, the area under the $i = f(t)$ curve can be integrated.

As working electrode DME can be used, in a special cell allowing a small volume (0.5 to 1.0 ml) to be electrolyzed in a solution stirred by the falling off mercury drops. Such electrolysis takes 8 – 12 hours to carry out, under strictly anaerobic conditions. This approach eliminates surface reactions, but consecutive bulk reactions can convert the primary electrolysis product.

When a Hg-pool electrode is used, typically 30 – 100 ml of the solution is used and the solution is vigorously stirred, preferably with a magnetic stirrer located in the Hg-pool. The electrolysis time is typically between 30 and 300 min.

Much faster electrolyses can be carried out when a HMDE is used — typically during 5 to 300 s. There is much less experimental evidence available for this type of coulometry to offer unbiased evaluation.

Product identification and yield are excellent proofs of the value of "n". For example, an alcohol is formed from an aldehyde or a ketone only by a two-electron process. It is nevertheless important to prove that identified species really is the predominant product.

Confirmation of the Nature of the Type of the Process Involved

For the use of currents in elucidation of the scheme of the electrode process, it is essential to understand the nature of the process controlling the limiting current. Variation of currents with concentration enables separation of some categories, as mentioned above. Further information can be obtained by varying the pressure of mercury, using a naturally dropping electrode, varying deliberately the drop-time or recording current-voltage curves during the life of a single mercury drop.

Using a natural DME and measuring the mean current (i.e. the current at the center of oscillations, for which theoretical expressions were derived, rather than the top of oscillations, which can significantly differ from theoretical "maximum current") at various heights of the mercury reservoir ("h" being the distance between the tip of the capillary and level of mercury in the reservoir, corrected for "back pressure" $H_{back} = 3.1\, m^{1/3} t_1^{1/3}$, where m is the outflow velocity of mercury and t_1 the drop-time, which is typically 1 – 2 cm), plots of $i_{\lim}$ as a function of "h" can be obtained (Fig. 3). If the plot of $i_{\lim} = f(\sqrt{h})$ is linear and the extrapolated line passes through the origin (Fig. 3a), the current is diffusion controlled. If the current is directly proportional to "h" (Fig. 3b), it is governed by adsorption (i_a). And finally, if the current is independent of "h" (Fig. 3c), it is governed by the rate of a chemical reaction preceding the electron transfer and is denoted kinetic current (i_k).

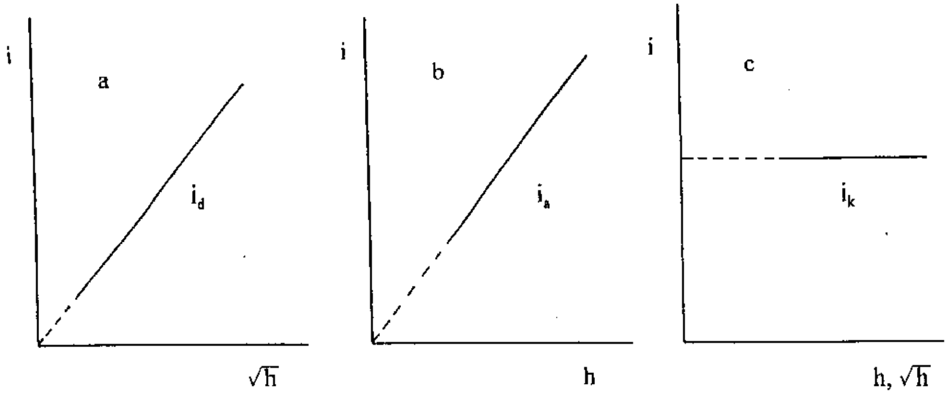


Fig. 3 Dependence of the limiting current (i) on the height of the mercury column (h): (a) Diffusion current; (b) adsorption current; (c) kinetic current

There is one group of currents which is not clearly identified by dependences on "c" and "h"; those are catalytic currents. Such currents can show plots resembling Figs. 3a, 3b, or 3c. Only when a current increases with decreasing "h", it is definitely one type of catalytic current. There are two main large groups of catalytic currents: Those which involve catalytic evolution of hydrogen and those in which the electrolysis product is chemically reoxidized or re-reduced yielding the starting material. The first group of catalytic waves, which often have a shape of a peak in dc polarography, increases prominently with decreasing pH (Fig. 4a) and increases at a given pH in a buffer with increasing concentration of the buffer (Fig. 4b). For currents where the electroactive species is regenerated by the catalyst (or mediator), the current is a function of the square-root of concentration of the catalyst (Fig. 4c).

Using the dependence of the mean current on the drop-time or the instanta-

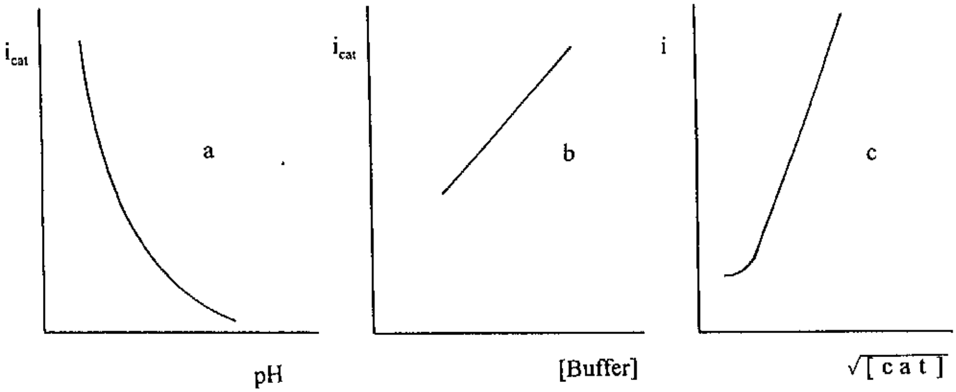


Fig. 4 Characteristics of catalytic currents: (a) and (b) currents of catalytic hydrogen evolution; (c) currents of system where the electroactive species is regenerated by an oxidation-reduction process. (a) Dependence on pH; (b) dependence on buffer concentration; (c) dependence on concentration of the catalyst

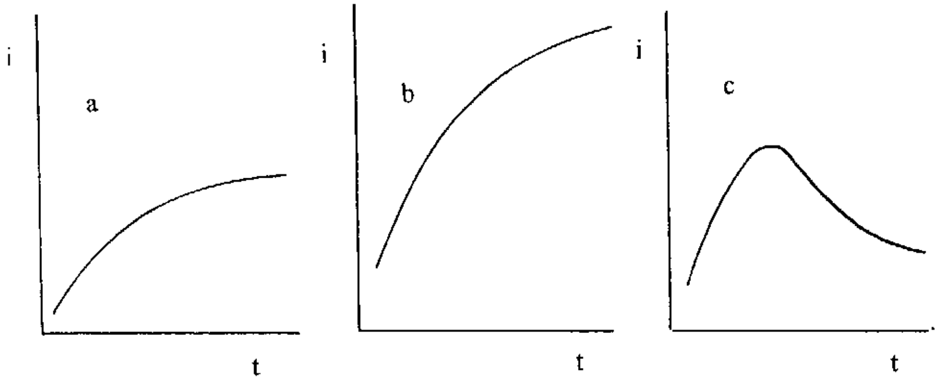


Fig. 5 Changes of instantaneous current on a single drop on time or of the mean current on drop time: (a) Diffusion current; (b) kinetic current; (c) adsorption current

neous current on the time (on a single drop), the diffusion current increases in a 1/6th parabola (Fig. 5a), kinetic in a 2/3rd parabola (Fig. 5b) and adsorption currents show an increase, followed by a decrease after the time the surface of the electrode is covered by the adsorbed form (Fig. 5c). To distinguish between i_d and i_k, $\log i = f(t)$ plot is simplest: for i_d the slope of the linear plot is about 0.18, for i_k about 0.66 (Fig. 6).

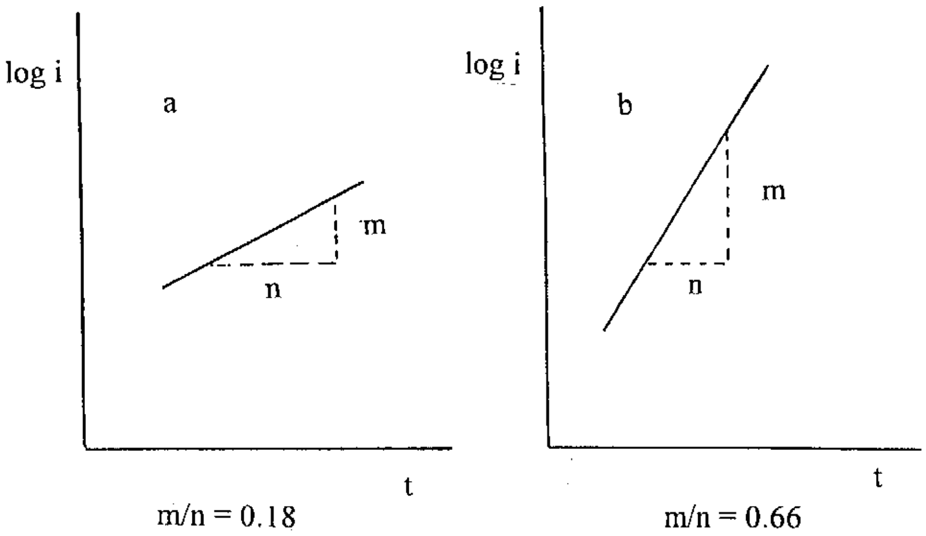


Fig. 6 Distinguishing between diffusion and kinetic instantaneous current using $\log i = f(t)$: (a) Diffusion current, slope 0.18; (b) kinetic current, slope 0.66

Role of Acid-Base Equilibria and Other Acid-Base Catalyzed Reactions Accompanying the Electron Transfer

Electron transfers in protic systems are often accompanied by proton transfers. If such proton transfers occur before the electron transfer in a reversible or irreversible process (see below) or if a proton transfer follows a reversible one- or two-electron process, the presence of acid-base processes can be identified and their nature recognized based on dependence of polarographic half-wave potentials and sometimes limiting currents with pH. If, on the other hand, the proton transfer occurs following an irreversible electrode process, polarography usually does not offer any information concerning such a process. For example, in the reduction of some aryl bromides the following sequence takes place

$$\mathrm{ArBr} + \mathrm{e} \rightleftharpoons \mathrm{ArBr}^- \tag{1}$$

$$\mathrm{ArBr}^- \Rightarrow \mathrm{Ar}^{\bullet} + \mathrm{Br}^- \tag{2}$$

$$Ar^{\bullet} + e \Rightarrow Ar^{-} \tag{3}$$

$$Ar^{-} + H^{+} \leftrightharpoons ArH \tag{4}$$

As at least step (2) is not extremely fast and neither is the protonation of the carbanion in reaction (4), neither the half-wave potentials nor the limiting currents of the reduction of such aryl bromides are pH dependent.

For all other systems to obtain information about acid-base equilibria and other chemical reactions involved, a detailed pH-dependence of polarographic curves over the entire pH range, in which the compound is electroactive, should be followed. For this purpose current-voltage curves in 0.05 to 0.2 mM solutions of the studied compound in buffers differing by 0.5 pH-units or less are recorded. Simple buffers are preferred to universal (mixed) buffers, as sometimes buffer components also play a role of proton donors. Buffers must have sufficient buffering capacity — the concentration of the buffer component (either the acid or the base) present in lower concentration must be at least 20 times higher than that of the studied species. 0.05 to 0.1 M buffer components are most frequently used. It is preferable to keep ionic strength constant by addition of a neutral salt — perchlorates and in some instances nitrates are generally preferred to chlorides, which may affect electrode processes. For all current-voltage curves recorded, mean limiting currents and half-wave potentials are measured and plotted as a function of pH.

A general rule should be stated first: Empirically it has been observed that if a simple acid-base equilibrium precedes the first electron uptake, the conjugate acid is *always* reduced at more positive potentials (i.e. easier) than its conjugate base. This is independent of the initial charge of the acid component and applies to couples like

$$H_2A \rightleftharpoons HA^{-} + H^{+} \tag{5}$$

$$HA^{-} \rightleftharpoons A^{2-} + H^{+} \tag{6}$$

or

$$BH_2^{2+} \rightleftharpoons BH^+ + H^+ \tag{7}$$

$$BH^+ \rightleftharpoons B + H^+ \tag{8}$$

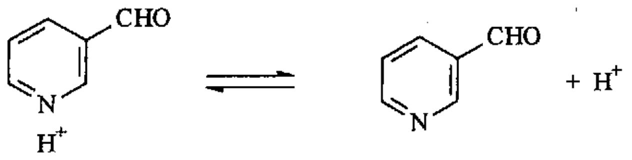
where the species on the left-hand side is more easily reduced.

Examples of reducible acids:

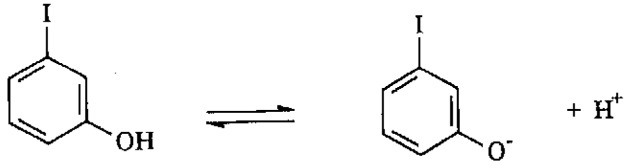
$$CH_3COCOOH \rightleftharpoons CH_3COO^- + H^+ \tag{9}$$

$$HOOCCH{=}CHCOOH \rightleftharpoons HOOCCH{=}CHCOO^- + H^+ \tag{10}$$

$$HOOCCH{=}CHCOO^- \rightleftharpoons {}^-OOCCH{=}CHCOO^- + H^+ \tag{11}$$



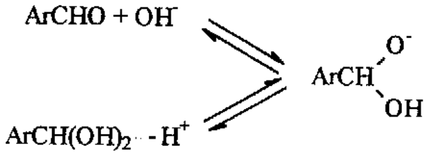
(12)



(13)

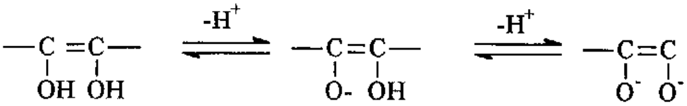
In contrast, the conjugate base is *always* more easily oxidized (i.e. at more negative potentials) than its conjugate acid. Thus in couples (5) – (8), HA^-, A^{2-}, BH^+, and B are the more easily oxidized species.

Examples:



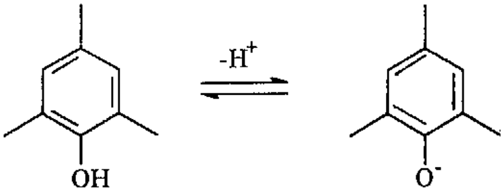
$$\mathrm{ArCHO} + \mathrm{OH^-} \rightleftharpoons \mathrm{ArCH(O^-)(OH)} \rightleftharpoons \mathrm{ArCH(OH)_2} - \mathrm{H^+}$$

(14)



$$-\mathrm{C(OH)=C(OH)}- \xrightleftharpoons{-\mathrm{H^+}} -\mathrm{C(O^-)=C(OH)}- \xrightleftharpoons{-\mathrm{H^+}} -\mathrm{C(O^-)=C(O^-)}$$

(15)



(16)

Conjugate bases on the right hand side of equations (14) – (16) are the more easily oxidized form.

In the following it will be shown how it is possible from variations of limiting currents and half-wave potentials to conclude on processes involved. Individual systems will be discussed starting from simpler and proceeding to more complex ones.

a) Constant limiting current, half-wave potential pH-dependent

The interpretation of experimental data in this case depends on the reversibility of the system (for definition and checks on reversibility see below).

(A) *Reduction of reversible systems*

Whereas limiting current remains pH-independent (Fig. 7a), the dependence of half-wave potentials shows several linear segments with varying slopes corresponding to $dE_{1/2}/d\mathrm{pH} = pRT/nF$, at 25 °C hence $dE_{1/2}/d\mathrm{pH} = p0.059/n$ (where "p" is the number of protons transferred and "n" the number of electrons). The value of "p" corresponds to the difference between the number of protons in the electroactive form and the number of protons in the form predominating in the solution in the given pH-range.

The pH at the intersection of the two linear segments corresponds to a $\mathrm{p}K_a$

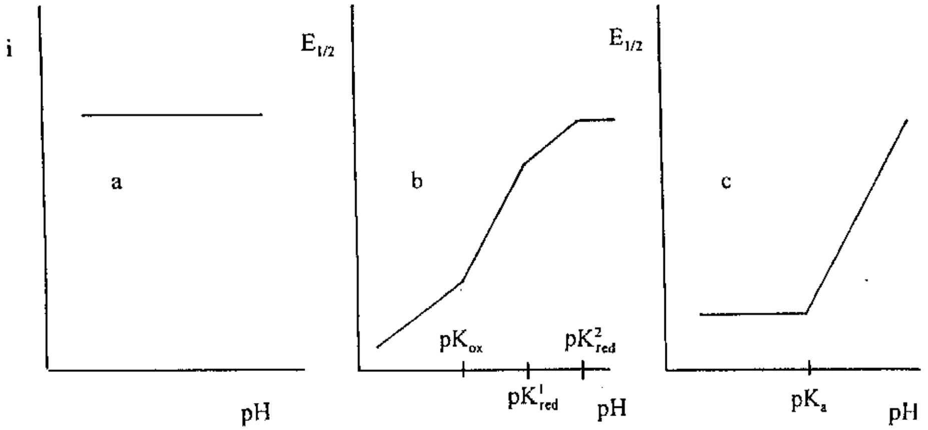
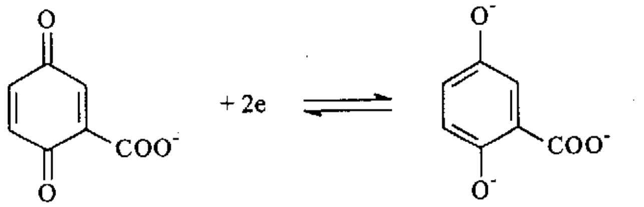


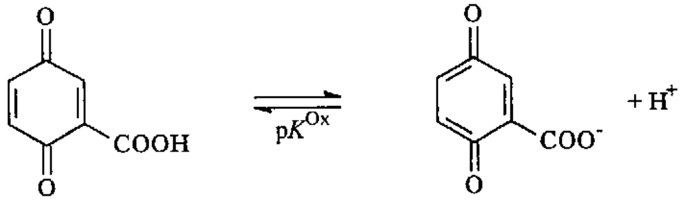
Fig. 7 Reduction of systems where the limiting current is pH independent (a): Dependence of $E_{1/2}$ on pH for (b) reversible systems; (c) irreversible systems

value. If the slope of $dE_{1/2}/d\text{pH}$ for the segment at lower pH value is smaller than the slope $dE_{1/2}/d\text{pH}$ for the segment at higher pH values (hence if in the plot the slope increases) the intersection corresponds to a pK_a value of the oxidized form (pK^{Ox}). If the slope of the plot ($dE_{1/2}/d\text{pH}$) decreases, the intersection corresponds to a dissociation of the reduced form (pK^{Red}).

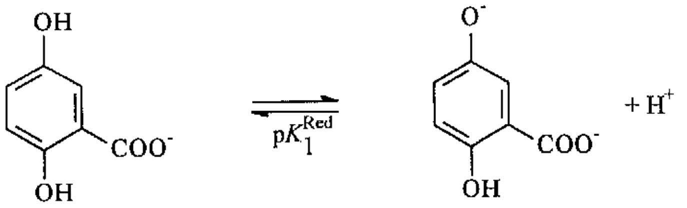
For example for the 2-carboxy-1,4-benzoquinone (Fig. 7b)



(17)



(18)



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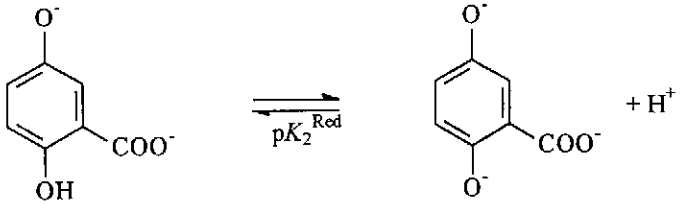


(20)

the intersection of segments with $dE_{1/2}/d\mathrm{pH} = 0.029\ \mathrm{V\,pH^{-1}}$ and that with $dE_{1/2}/d\mathrm{pH} = 0.060\ \mathrm{V\,pH^{-1}}$ corresponds to $\mathrm{p}K^{Ox}$ of Eq. (18), the intersection of segments with slopes $0.060\ \mathrm{V\,pH^{-1}}$ and $0.029\ \mathrm{V\,pH^{-1}}$ corresponds to $\mathrm{p}K_1^{Red}$ of Eq. (19) and the intersection of segments with slopes $0.029\ \mathrm{V\,pH^{-1}}$ and $0.000\ \mathrm{V\,pH^{-1}}$ to $\mathrm{p}K_2^{Red}$ of Eq. (20).

(B) Reduction of irreversible systems

For such systems where over the entire accessible pH range the limiting current of an irreversible reduction remains pH independent (Fig. 7a) and the dependence of half-wave potentials on pH shows two linear segments with $dE_{1/2}/d\mathrm{pH} = 0$ and $dE_{1/2}/d\mathrm{pH} = pRT/\alpha nF$, (Fig. 7c), the pH value at the intersection of these segments corresponds to $\mathrm{p}K_a$ of an acid-base reaction of the oxidized form.

An example of a system that follows such pattern is the reduction of phenacylsufonium cations

$$\mathrm{PhCOCH_2\overset{+}{S}R_2} \underset{\mathrm{p}K_a^{Ox}}{\rightleftharpoons} \mathrm{PhCO\overset{-}{C}H\overset{+}{S}R_2} + \mathrm{H^+} \tag{21}$$

$$\mathrm{PhCOCH_2\overset{+}{S}R_2} + 2\mathrm{e} \longrightarrow \mathrm{PhCOCH_2^-} + \mathrm{R_2S} \tag{22}$$

$$\mathrm{PhCOCH_2^- + H^+ \rightleftharpoons PhCOCH_3} \qquad (23)$$

For this system the intersection of the two linear segments at pH 7.2 corresponds to pK_a of reaction (21). The constant value of the limiting current at least up to pH 12 and the shift of $E_{1/2}$ in the same pH-range indicates that equilibrium (21) remains rapidly established (compared to the rate of electroreduction) and the zwitterion is rapidly protonated to replace the reduced cation in reaction (22) at least up to pH 12.

(C) *Oxidations of irreversible systems*

When the limiting current remains pH independent (Fig. 8a) and the half-wave potentials are shifted to more negative values and the $E_{1/2} = f(\mathrm{pH})$ plot shows two linear segments with $dE_{1/2}/d\mathrm{pH} = pRT/\alpha nF$ and 0.0 V pH^{-1}, the oxidation corresponds to a loss of "*n*" electrons by the conjugate base and involves an antecedent rapidly established acid-base equilibrium. The pH at the intersection of two linear segments of the plot (Fig. 8b) corresponds to pK_a of the reduced form (pK^{Red}). Such behavior is observed for example in the oxidation of the enediol grouping of the ascorbic acid (24) and (25)

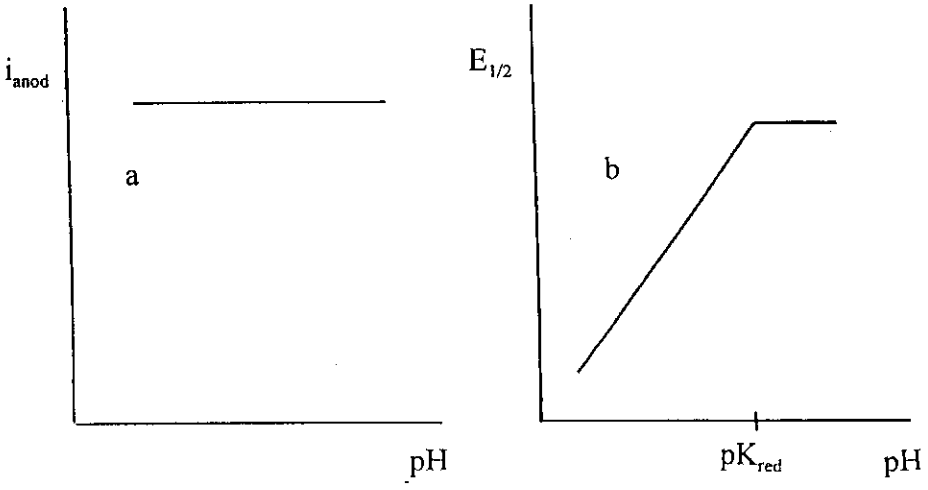
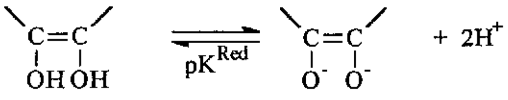
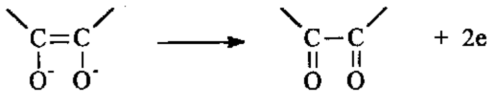


Fig. 8 Oxidation of irreversible systems where the limiting current is pH independent (a). Dependence of $E_{1/2}$ on pH (b)



$$\mathrm{>C(OH){=}C(OH)<} \underset{\mathrm{p}K^{Red}}{\rightleftharpoons} \mathrm{>C(O^-){=}C(O^-)<} + 2\mathrm{H}^+ \qquad (24)$$



(25)

The resulting α-diketone undergoes rapid addition of water to one of the carbonyl groups.

b) Systems in which both the limiting currents and the half-wave potentials are a function of pH

The systems in which both the limiting current and half-wave potential vary with pH will be discussed here using the shape of the $i = f(\text{pH})$ plot for classification.

(A) *With increasing pH a cathodic wave decreases completely*

One of the most frequently encountered types of pH dependences results in a cathodic wave that decreases with increasing pH above a certain pH value (Fig. 9a). The plot of the decrease of this wave (i_1) as a function of pH has a shape of a dissociation curve (Figs 9b and 9c). If the conjugate base is reducible within the accessible potential range, its wave (i_2) increases with increasing pH. If the acid and conjugate base are reduced by the same number of electrons ($n = m$), the sum of $i_1 + i_2$ remains constant.

Such patterns correspond to a sequence (26) – (28)

$$\text{HA} \underset{k_r}{\rightleftharpoons} \text{A}^- + \text{H}^+ \qquad (26)$$

$$\text{HA} + n\text{e} \rightarrow \text{P}_1 \qquad i_1 \qquad (27)$$

$$\text{A}^- + m\text{e} \rightarrow \text{P}_2 \qquad i_2 \qquad (28)$$

(The conjugate acid denoted HA can be an uncharged molecule, a cation or an anion.)

There are two distinct groups of such variations of wave-heights with pH, depending on the rate of establishment of the equilibrium (26)

I) Slowly established equilibrium

When equilibrium (26) is slowly established as compared to the rate of reduction, the limiting current at each pH is proportional to concentration of the species in the

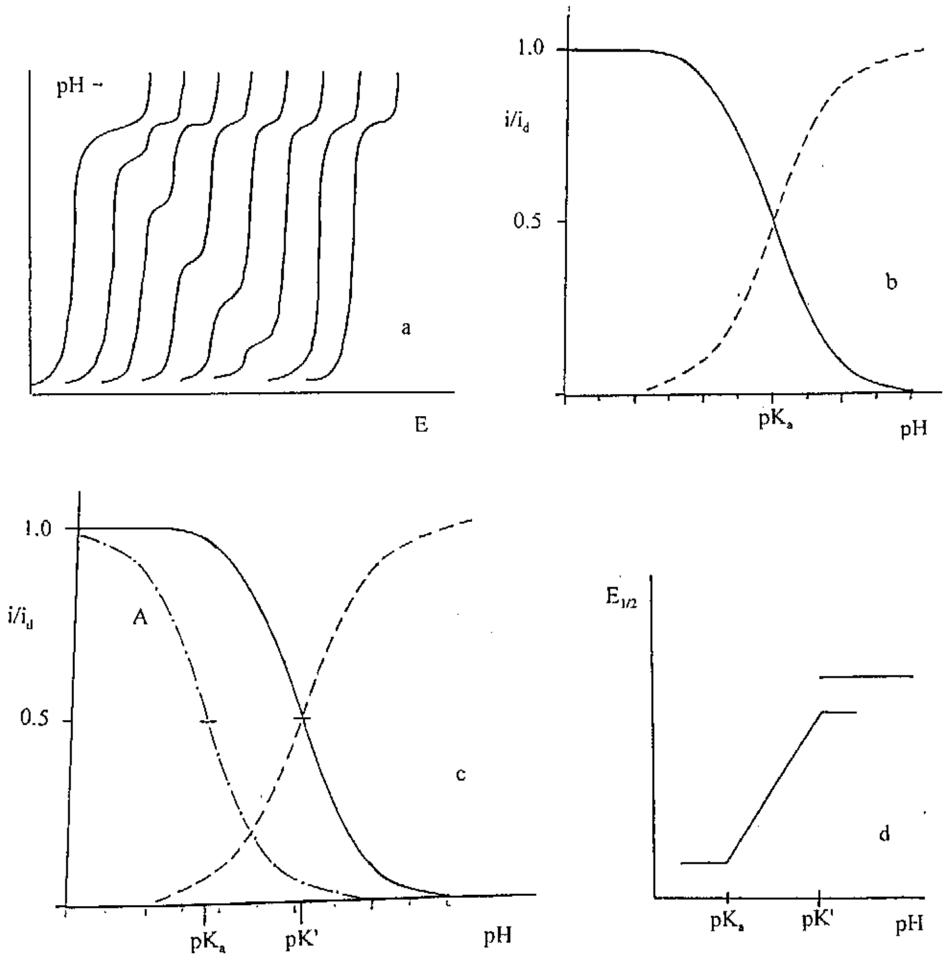
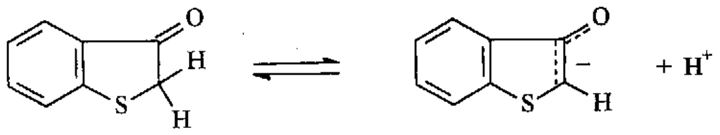


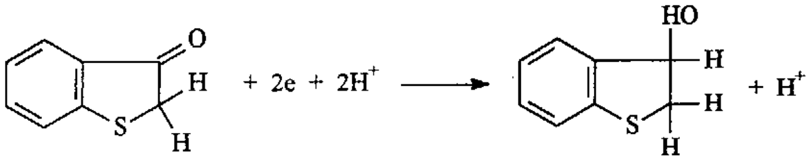
Fig. 9 Reduction of systems where half-wave potentials depend on pH and limiting current of an acid form decreases with increasing pH to zero: (a) pH dependence of current-voltage curves; (b) pH dependence of limiting currents for slowly established acid-base equilibria; (c) pH dependence of current of the conjugate acid (····), of the conjugate base (– – – – –) and of the absorbance A (–·–·–·); (d) pH dependence of $E_{1/2}$ of the conjugate acid and base (at more negative potentials)

solution, to [HA] for i_1 and [A$^-$]] for i_2. In this case the limiting current at each pH is diffusion controlled (as shown on linear dependence on $\sqrt{h}$, see above). For such system the inflection point of the i_{lim} = f(pH) plot occurs at pH = pK_a (Fig. 9b). Hence this inflection point, denoted pK', is in this case equal to pK_a obtained at equilibrium, using spectrophotometry or titration.

An example of such system is the reduction of 3-thionaphthenone (29) – (30)

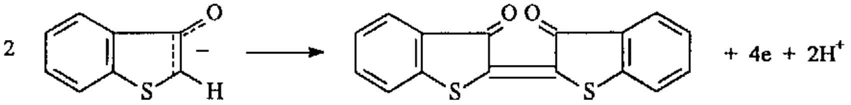


(29)



(30)

In this case the conjugate base, the carbanion, is reduced at too negative potentials to be followed, but yields an anodic wave, corresponding to oxidation (31)



(31)

II) Rapidly established equilibrium

Much more frequently encountered are systems in which the rate of establishment of equilibrium (26) is comparable with the rate of reduction in (27). In this case, as in the previous one, a decrease of i_1 is observed as in Fig. 9a. There are, nevertheless, two differences: The wave i_1 is kinetic, which can best be proved when $i_1/i_{\lim} \leq 0.15$ from independence of i_1 of h (see Fig. 3c). Furthermore, pH at the inflexion point of $i_1 = f(\text{pH})$, where $i_1 = i_{\lim}/2$, which is denoted pK', is larger than the value of pK_a determined by spectrophotometry or potentiometry. This is due to the following: At pH$_1$ (Fig. 9c), which is below pK_a (equilibrium concentration of HA in Fig. 9c is indicated by dotted line and the pH at its inflexion point is equal pK_a), form HA predominates in the solution and is reduced. Current i_1 is equal to $i_{\lim}$ and, as the same form which predominates is reduced, $(E_{1/2})_1$ at pH < pK_a is constant (Fig. 9d). At pH > pK_a , form A$^-$ predominates in the solution, but as long as the rate of protonation of A$^-$ in Eq. (26) with rate constant k_r is so high that all of A$^-$ is converted during the life of a drop into HA (which is continuously reduced) i_1 remains equal to $i_{\lim}$ (Fig. 9c). As HA is reduced, but must be formed by protonation, $(E_{1/2})_1$ in this pH range, where reaction with k_r is fast, is shifted with increasing pH to more negative values (Fig. 9d).

With increasing pH the rate of protonation with constant k_r (which is a linear function of [H$^+$] decreases. At sufficiently high pH, all of A$^-$ cannot be converted into HA. In this pH range i_1 decreases and it can be shown that $i_1 = f(\mathrm{pH})$ must have a shape of a dissociation curve of a monobasic acid. The value of pH where $i_1 = i_{\mathrm{lim}}/2$ is denoted pK' and represents the inflexion point of the dissociation curve. At pH > pK' the half-wave potential of wave i_1 becomes pH independent (Fig. 9d).

As the rate of protonation of A^- decreases, current i_2 increases. In numerous instances reduction of A^- does not involve a proton transfer prior to the potential determining electron transfer and hence $(E_{1/2})_2$ is pH independent. If the species reduced in i_2 is an anion, its half-wave potential can be, nevertheless, dependent on nature and concentration of supporting electrolytes.

Example of a system where both the acid and base form are reduced is the reduction of phenylglyoxylic acid

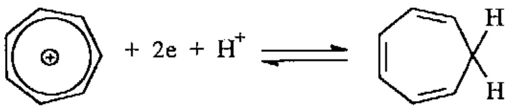
$$\mathrm{PhCOCOOH} \underset{K_a}{\rightleftharpoons} \mathrm{PhCOCOO^-} + \mathrm{H^+} \tag{32}$$

$$\mathrm{PhCOCOOH} + 2\mathrm{e} + 2\mathrm{H^+} \xrightarrow[i_1]{} \mathrm{PhCH(OH)COOH} \tag{33}$$

$$\mathrm{PhCOCOO^-} + 2\mathrm{e} + 2\mathrm{H^+} \xrightarrow[i_2]{} \mathrm{PhCH(OH)COO^-} \tag{34}$$

An example of an acid-base equilibrium, where the conjugate base is reduced at so negative potentials that only i_1 is observed, is the reduction of tropylium ion

(35)



(36)

B) *With increasing pH a cathodic wave decreases to one half of the original height*

In some instances the limiting current does not decrease with increasing pH completely, but reaches a limiting value, which can be 75%, 50% or 25% of the initial current. Most frequently the decrease of a two-electron reduction wave to a one-electron reduction wave is observed. Such dependence on pH corresponds to scheme (37) – (40)

$$\left.\begin{array}{l}\left.\begin{array}{ll}\mathrm{A} + \mathrm{e} \underset{E_{37}}{\rightleftharpoons} \mathrm{A}^{\bullet -} & (37)\\ \mathrm{A}^{\bullet -} + \mathrm{H}^{+} \rightleftharpoons \mathrm{HA}^{\bullet} & (38)\end{array}\right\} i_{1a}\\ \begin{array}{ll}\mathrm{HA}^{\bullet} + \mathrm{e} \underset{E_{39}}{\rightarrow} \mathrm{HA}^{-} & (39)\\ \mathrm{HA}^{-} + \mathrm{H}^{+} \rightleftharpoons \mathrm{H_2A} & (40)\end{array}\end{array}\right\} i_1$$

$$\left.\begin{array}{ll}\mathrm{A}^{\bullet -} + \mathrm{e} \underset{E_{41}}{\rightarrow} \mathrm{A}^{2-} & (41)\\ \mathrm{A}^{2-} + 2\mathrm{H}^{+} \rightleftharpoons \mathrm{H_2A} & (42)\end{array}\right\} i_2$$

Such scheme is manifested by the decrease of i_1 (Fig. 10). As long as the rate of protonation of the radical anion A^- in reaction (38) is fast enough to convert all of A^- into HA•, the height of wave i_1 remains constant and corresponds to a two-electron process. This is due to the fact that potential E_{39} is always more positive than potential E_{37}. With increasing pH the rate of protonation in reaction (38) decreases. The plot of $i_1 = f(\mathrm{pH})$ has a shape of a dissociation curve (Fig. 10) with a limiting value (i_{1a}), which corresponds to a transfer of a single electron in reaction (37).

In some instances, reduction of A^- occurs at more negative potentials E_{41} in

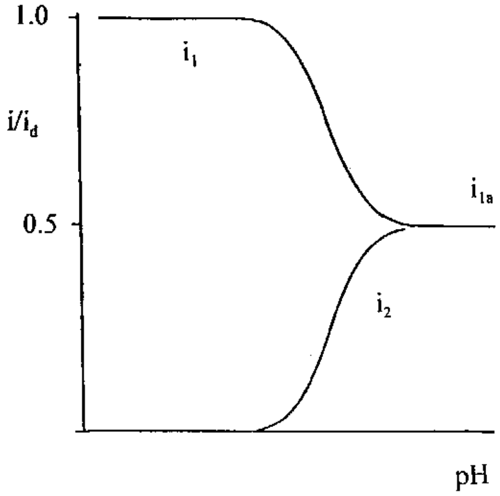


Fig. 10 Reduction of systems where the limiting current decreases to one half of its original value. More positive wave i_1 decreases to one half (i_{1a}), more negative wave i_2 increases

wave i_2, the height of which increases with increasing pH (Fig. 10) until it reaches a value corresponding to a one-electron transfer.

As neither in reaction (37) nor (41) the proton transfer occurs before the transfer of the potential-determining first electron, the half-wave potentials of i_1, i_{1a} and i_2 remain pH independent, but $(E_{1/2})_2$, which corresponds to reduction of an anionic species, depends on nature and concentration of cations of the supporting electrolyte.

Examples of such behavior are reductions of aromatic aldehydes and aryl alkyl ketones at pH > 9, which e.g. for acetophenone follows the pattern

$$\mathrm{PhCOCH_3 + e \rightleftharpoons Ar\overset{\bar{\cdot}}{C}OCH_3} \qquad (43)$$

$$\mathrm{Ph\overset{\bar{\cdot}}{C}OCH_3 + H^+ \rightleftharpoons Ph\dot{C}(OH)CH_3} \qquad (44)$$

$$\mathrm{Ph\dot{C}(OH)CH_3 + e \rightarrow Ph\bar{C}(OH)CH_3} \qquad (45)$$

$$Ph\bar{C}(OH)CH_3 + H^+ \rightleftharpoons PhCH(OH)CH_3 \tag{46}$$

$$Ph\overset{\bar{\cdot}}{C}OCH_3 + e \rightarrow Ph\overset{2-}{\dot{C}}OCH_3 \tag{47}$$

$$Ph\overset{2-}{\dot{C}}OCH_3 + 2H^+ \rightleftharpoons PhCH(OH)CH_3 \tag{48}$$

C) *Cathodic wave decreases over a region of pH to a fraction of its original height*

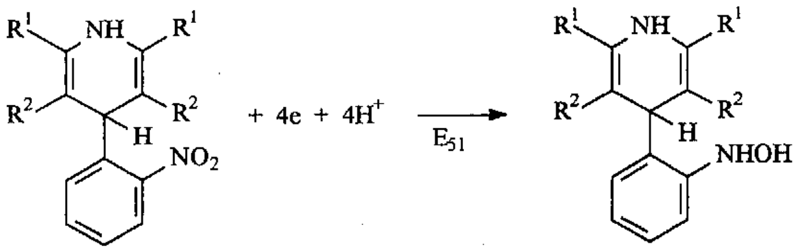
In some instances the limiting current decreases below the value corresponding to a diffusion-controlled current which involves transfer of "*n*" electrons. The plots of $i = f(\mathrm{pH})$ can have shapes shown in Fig. 11. In all the cases the following scheme is involved in which the electroactive form A is in equilibrium with an electroinactive form

$$A \underset{v}{\rightleftharpoons} \text{Electroinactive form} \tag{49}$$

$$A + ne \rightarrow P_1 \tag{50}$$

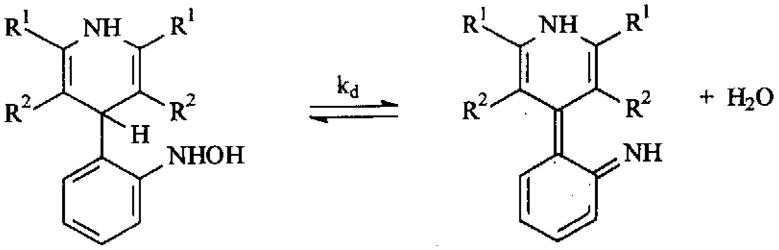
If reaction (49) is acid catalyzed, the dependence in Fig. 10a is observed, if it is base catalyzed, corresponding plot is given in Fig. 10b, and if it is both acid and base catalyzed, it is shown in Fig. 10c.

Examples of an acid catalyzed reaction are the reduction of nifedipine (51) – (53) and metamitron (54) – (55)

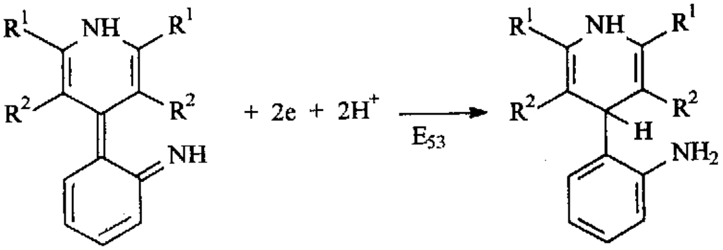


(51)

$R^1 = CH_3$
$R^2 = COOCH_3$



(52)



(53)

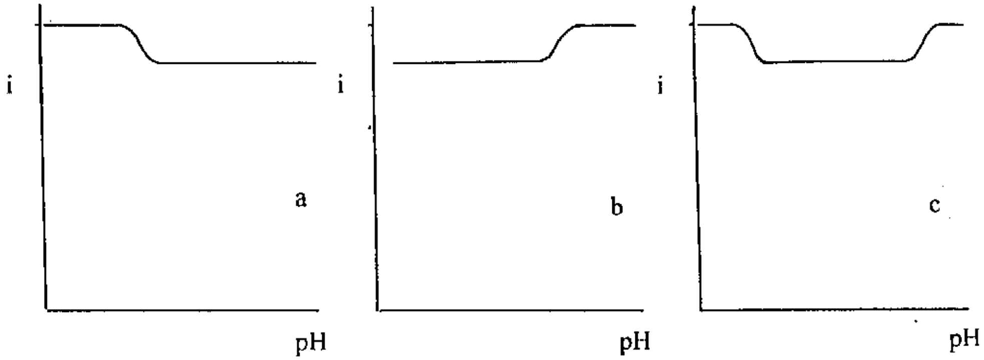
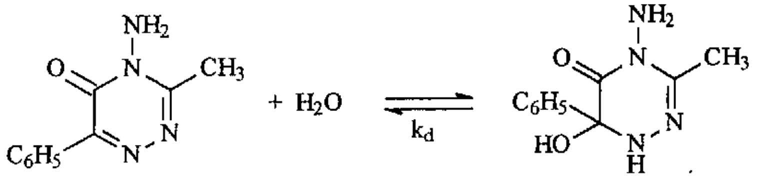


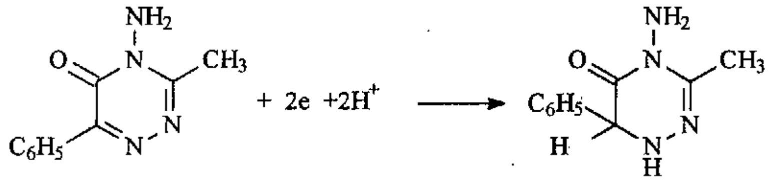
Fig. 11 Reduction of systems involving equilibria between the electroactive and inactive form, for example involving covalent hydration of C=O or C=N bonds: (a) Acid catalyzed dehydration; (b) base catalyzed dehydration; (c) acid and base catalyzed dehydration

The dehydration in reaction (52) with rate constant k_d is acid catalyzed. Therefore the limiting current increases with decreasing pH as in Fig. 10a. As potential E_{53} is more positive than E_{51}, only a single six-electron wave is observed in strongly acidic media.

Metamitron is a pesticide containing 1,2,4-triazine ring. In this compound 1,6-azomethine bond is reduced in protonated form in the first step. But the 1,6-azomethine bond also can add water and alcohols in a nucleophilic process



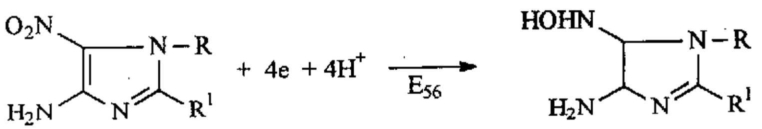
(54)



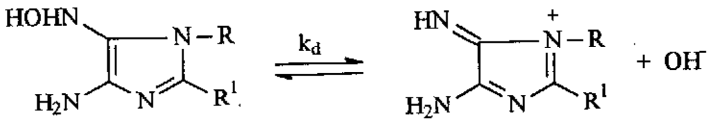
(55)

The dehydration in reverse reaction (54) with rate constant k_d is acid catalyzed, and hence pH dependence as shown in Fig. 10a.

An example of base-catalyzed dehydration is the reduction of 1-alkyl-4-amino-5-nitroimidazoles (56) – (58)



(56)



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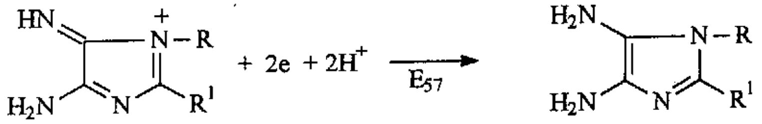
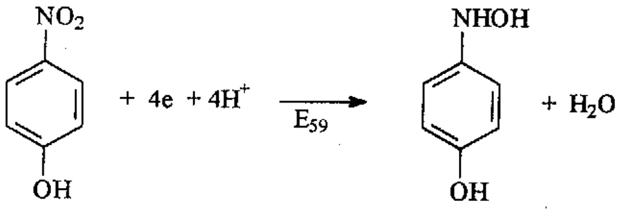


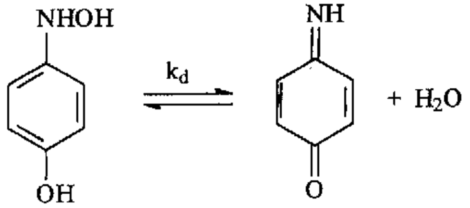
(58)

As E_{57} is more positive than E_{56}, in sufficiently basic solution, where the base catalyzed dehydration (57) with rate constant k_d is sufficiently fast, a single six-electron wave is observed.

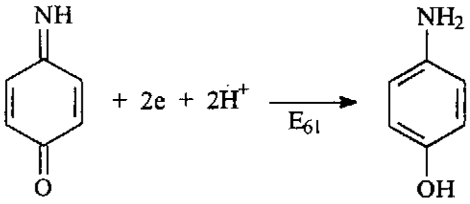
Finally, an example where dehydration reaction is both acid and base catalyzed and where the $i_{\text{lim}} = f(\text{pH})$ plot resembles that in Fig. 10c is the reduction of *p*-nitrophenol (59) – (61)



(59)



(60)



(61)

As potential E_{61} is more positive than E_{59}, a single six-electron wave, corresponding to formation of *p*-aminophenol, is observed in sufficiently strong acidic or alkaline media. Dehydration reaction (60) with rate constant k_d is both acid and base catalyzed.

It might be pointed out that the current in the medium pH range (where it is pH independent) is not a simple function of the concentration of the nonhydrated form, as the current is also affected by the rate of solvent-catalyzed dehydration.

D) *Cathodic currents which with increasing pH first increase, then decrease*

A dependence of current, which with increasing pH first increases and then decreases (Fig. 12) indicates that electroreduction is accompanied by two reactions:

The yield of the first reaction is favored with an increase in pH, the yield of the second one oppositely decreases with increasing pH. The two reactions may be either two consecutive acid-base equilibria or formation of an electroactive species by a base-catalyzed reaction followed by a nucleophilic addition which decreases the concentration of the electroactive species.

I) Diprotic acids

Dependence of the limiting current on pH shown in Fig. 12 is observed for the reduction of a monoanion of a dibasic acid, following scheme (62) – (64)

$$\mathrm{H_2A} \rightleftarrows \mathrm{HA^-} + \mathrm{H^+} \tag{62}$$

$$\mathrm{HA^-} \rightleftarrows \mathrm{A^{2-}} + \mathrm{H^+} \tag{63}$$

$$\mathrm{HA^-} + n\mathrm{e} \rightarrow \mathrm{P} \tag{64}$$

Examples can be reductions of maleic or fumaric acid and reduction of pyridoxal. For ethylene dicarboxylic acids the relevant scheme is (65) – (67)

$$\mathrm{HOCCH{=}CHCOOH} \rightleftarrows \mathrm{HOOCCH{=}CHCOO^-} + \mathrm{H^+} \tag{65}$$

$$\mathrm{HOOCCH{=}CHCOO^-} \rightleftarrows \mathrm{{}^-OOCCH{=}CHCOO^-} \tag{66}$$

$$\mathrm{HOOCCH{=}CHCOO^-} + 2\mathrm{e} + 2\mathrm{H^+} \rightarrow \mathrm{HOOCCH_2CH_2COO^-} \tag{67}$$

and for pyridoxal (68) – (70)

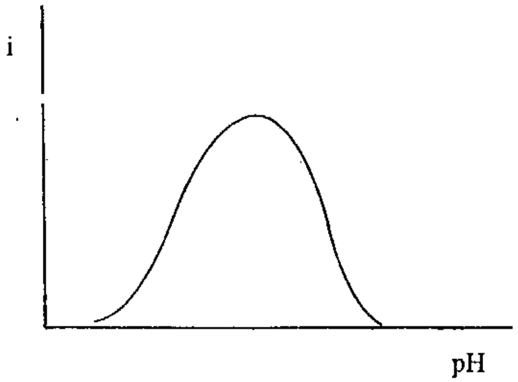
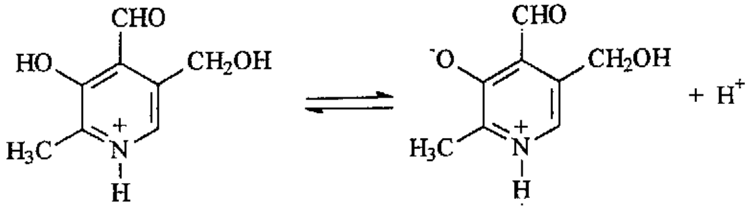
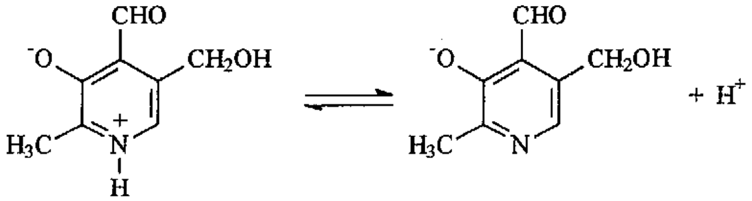


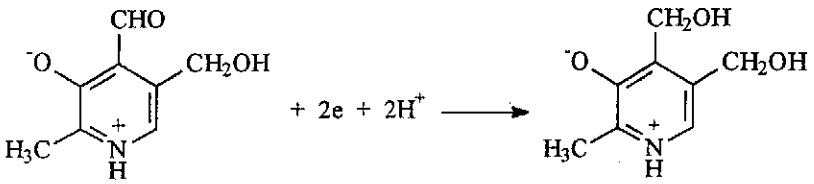
Fig. 12 Reduction of systems involving two pH dependent equilibria. The electroactive species is formed in a reaction with rate increasing with increasing pH and deactivated in a reaction with rate also increasing with increasing pH



(68)



(69)

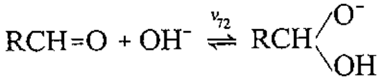


(70)

II) Reduction of aliphatic aldehydes accompanied by a base-catalyzed dehydration

Aliphatic aldehydes exist in aqueous solutions to a considerable extent as geminal diol derivatives. Their dehydration and formation of the electroactive unhydrated carbonyl form is base catalyzed. But in more strongly alkaline solutions OH^- ions add in a nucleophilic attack to the aldehyde forming a geminal diol anion, which is not reducible (but undergoes oxidation — see below). The chemical reactions involved can be described as (71) – (73)

$$RCH(OH_2) \overset{v_{71}}{\rightleftharpoons} RCH{=}O + H_2O \qquad (71)$$



$$RCH{=}O + OH^- \overset{v_{72}}{\rightleftharpoons} RCH\begin{matrix} O^- \\ OH \end{matrix} \qquad (72)$$

$$RCH{=}O + 2e + 2H^+ \rightarrow RCH_2OH \qquad (73)$$

The dehydration (v_{71}) is based catalyzed, its rate increases with increasing pH and hence the current corresponding to the reduction of the aldehyde (73) first increases. The rate of the addition of hydroxide ions (72) also increases with increasing pH. At a sufficiently high pH (and hence $[OH^-]$), the rate of nucleophilic addition (v_{72}) becomes larger than the rate of dehydration (v_{71}) and the number of reducible species (RCH=O) starts to decrease, which is manifested by the decrease in current at higher pH values.

E) *Increase of an anodic wave, corresponding to oxidation, with increasing pH*

For compounds where the electroactive conjugate base is formed in a reaction the rate of which increases with pH, the anodic wave increases with increasing pH. If the equilibrium yielding the base form undergoing oxidation is slowly established, as it was in the case of 3-thionaphthenone (see Section A) I), Eq. (31)) the decrease corresponds to the equilibrium constant. With a rapidly established acid base equilibrium, the anodic current increases with increasing pH (Fig. 13a). The $i_{anod} = f(\mathrm{pH})$ has a shape of an increasing dissociation curve, the pH at the inflexion (where $i_{anod} = i_{lim/2}$), denoted as pK', is smaller than pK_a The current for $i_{anod} < 0.15\, i_{lim}$ is kinetic, as shown by the independence of mercury pressure.

The plot of $E_{1/2} = f(\text{pH})$ shows three linear segments: pH independent at pH < $\text{p}K'$ and pH > $\text{p}K_a$, and shifted with a slope $dE_{1/2}/d\text{pH} = 0.059p/\alpha n$ (Fig. 13b), hence a completely mirror image when compared with graphs for reduction of the conjugate acid (Figs. 9c and 9d). Such plots as in Figs. 13a and 13b correspond to a system described in (74) and (75)

$$\begin{gathered}BH^+ \rightleftarrows B + H^+ \\ (\text{or } B + OH^- \rightleftarrows BOH^-)\end{gathered} \tag{74}$$

$$B\,(\text{or } BOH^-) \rightarrow P + ne \tag{75}$$

An example of this behaviour is the oxidation of aromatic aldehydes in alkaline solutions, which follows pattern (76) and (77)

$$ArCHO + OH^- \rightleftarrows ArCH(OH)O^- \tag{76}$$

$$ArCH(OH)O^- \rightarrow ArCOO^- + 2e + 2H^+ \tag{77}$$

Proofs of Reversibility

At the beginning of the discussion of the role of pH on polarographic waves the difference was pointed out between interpretation of $E_{1/2} = f(\text{pH})$ plots for reversible and irreversible systems.

Attention will be paid now to the definition of reversibility and the procedures used in proving that a given system at a given electrode can be described as reversible (or Nernstian).

A system is called reversible, if the equilibrium between the oxidized and reduced forms at the electrode surface is rapidly established.

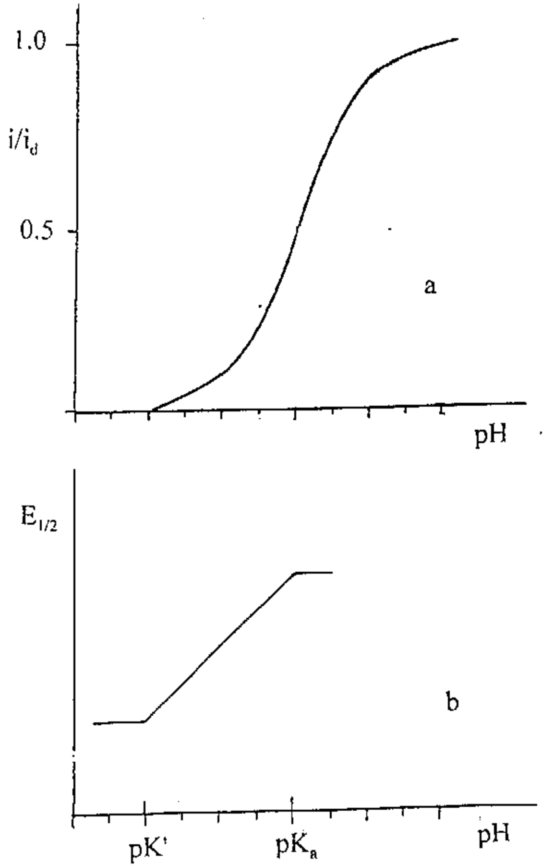


Fig. 13 Dependence of an anodic wave corresponding to oxidation of a conjugate base on pH: (a) Limiting anodic current; (b) half-wave potentials

The problem with the above definition is the meaning of "rapidly". The word used in this context is a so called "weasel word", that is a word which can have different meanings in different contexts. It is hardly meaningful to express the rate of the establishment of the equilibrium by a numerical value. It is usually defined relative to the time-window of the measurement. And as such time-window is different for different techniques, the reversibility as defined above depends on the technique used. The time window for individual techniques can be very roughly estimated as follows:

Potentiometry	10 s – min
Polarography	0.1 – 1.0 s
Linear sweep, or cyclic voltammetry	10^{-4} – 10^{-2} s

Reversibility of the overall chemical process depends a) on the rate of the electron transfer; b) on the rate of accompanying reactions which can involve the oxidized or the reduced form or both.

- a) When the electron transfer governs the reversibility, then
  - 1) when the time-window is short, the system is described as irreversible
  - 2) for larger time-windows the system can be described as reversible
- b) For a system where the reversibility depends on accompanying chemical reactions, then
  - 1) at a short time-window, the chemical reaction does not have time to alter the concentration of Ox and Red and the system can be denoted as reversible
  - 2) when the time-windows is larger, chemical reactions alter concentration of Red and Ox and the system is irreversible.

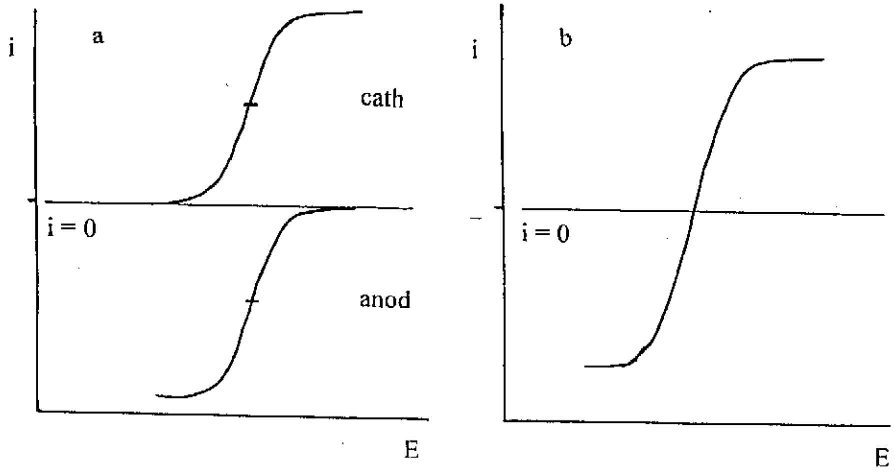


Fig. 14 Proof of reversibility under conditions of dc polarography: (a) Comparison of half-wave potentials of equimolar solutions of the oxidized (cathodic wave) and reduced form (anodic wave); (b) current-voltage curve of an equimolar mixture of the oxidized and reduced form

In dc polarography the proof of reversibility is based on comparison of the half-wave potentials of the oxidized and reduced forms. If $(E_{1/2})_{Ox}$ is practically equal to $(E_{1/2})_{Red}$ (as diffusion coefficients of these two forms usually are similar), such systems are called reversible (Fig. 14a). In such cases mixtures of the oxidized and the reduced forms (Fig. 14b) yield a single cathodic-anodic wave. Attempts to prove reversibility based on analysis of the shape of $i-E$ curves are unreliable: Even irreversible systems can have Nernstian shapes.

To obtain a proof that $(E_{1/2})_{Ox} = (E_{1/2})_{Red}$ by dc polarography, it is necessary to have both oxidized and reduced forms available. In some cases both these forms are stable and their solutions can be prepared from well defined chemicals (e.g. quinones and hydroquinones, aryl hydroxylamines and corresponding nitrosobenzenes). More often, nevertheless, the reduced form is not stable and readily undergoes autoxidation (by air oxygen). In such cases, after the curve of the reduction of the oxidized form was recorded, the reduction of the studied compound is carried out by a chemical reaction in the bulk of the solution. This can be achieved by purging the studied solution by hydrogen gas in the presence of some platinum or palladium catalyst (either colloidal or on a solid support). Some other reducing agents, like NH_2NH_2, $S_2O_3^{2-}$ or SO_3^{2-}, can sometimes be used but their possible reactivity as nucleophiles must be considered as well.

An alternative, instrumental approach is the use of the so-called Kalousek commutator. In this device, constant potential electrolysis is carried out over short time intervals and in following period the current of the electrolysis product is recorded as a function of the applied potential. The $i-E$ curve obtained in the absence of electrolysis (Fig. 15c, orig) is compared with the curve of the electrolysis product (Fig. 15c, commut). A similar principle is used in square wave polarography.

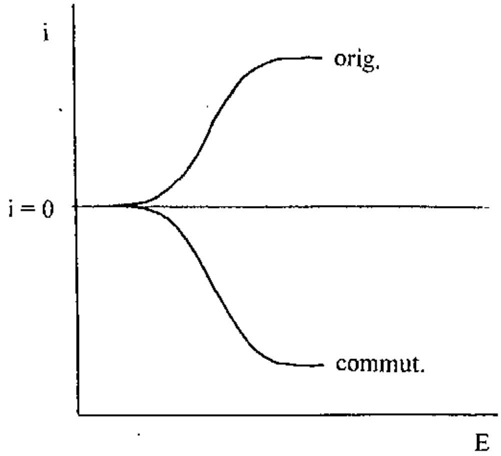


Fig. 15 Proof of reversibility of processes on the dropping mercury electrode using Kalousek commutator: Half-wave potentials of the reduction of the original solution of the oxidized form (orig.) are compared with those of the oxidation of the reduced form generated electrochemically in the commutator (commut.)

Another technique that can prove reversibility is cyclic voltammetry (CV), where a linearly increasing voltage ramp at rates varying usually between 5 mV s^{-1} and 1000 mV s^{-1} is applied to mercury electrode.

Most frequently a HMDE or a static mercury drop electrode are used for such measurements. To prove reversibility the system should show both a cathodic and an anodic peak. The cathodic and anodic peak currents should be approximately equal and the difference between potentials of the cathodic $(E_p)_c$ and anodic $(E_p)_a$ peaks should for reversible systems be equal to

$$\Delta E_p = (E_p)_c - (E_p)_a = 2\left(1.11\frac{RT}{nF}\right) \tag{78}$$

i.e. for $n = 1$ $\Delta E_p = 0.065$ V (at 25 °C) and for $n = 2$ $\Delta E_p = 0.033$ V. Furthermore, for a proper time-window (i.e. at neither too low nor too high rates of scanning), the value of E_p is independent of the rate of scanning and of concentration of the electroactive species.

There are some differences in conditions of electrolysis in dc polarography (which is practically a potentiostatic method) and in CV (where potential is always a function of time), but their discussion as well as the discussion of the use of CV in investigation of chemical reactions following electroactive species would be a topic of another communication.

As the above text was a content of a talk, references to literature sources are not given. The attached bibliography might enable those who are interested to find more details in original publications.

Bibliography of Petr Zuman
1945 – 1998

A. Publications in Journals

1. Zuman P.: Formation of Reducing Substances During the Heating of Sugar Solution, [in Czech] Listy Cukrovar. **62**, 81 (1945–46).
2. Zuman P.: The Influence of the Purification Methods on the Content of Reducing Substances in Sugar Solution, [in Czech] Listy Cukrovar. **62**, 89 (1945–46).
3. Zuman P.: Artificially Prepared Reductones, [in Czech] Listy Cukrovar. **62**, 97 (1945–46).
4. Zuman P.: Polarographic Behaviour of Acetone, Nature **175**, 585 (1950).
5. Zuman P.: The Reaction of Carbonyl Compounds with Primary Amines, [in German] Collect. Czech. Chem. Commun. **15**, 839 (1950).
6. Brdička R., Zuman P.: Polarographic Behaviour of Reductones and Coumarindiol, Collect. Czech. Chem. Commun. **15**, 766 (1950); [in Russian] Chimija **1**, 289 (1951).
7. Zuman P.: A List of Half-Wave Potentials, Collect. Czech. Chem. Commun. **15**, 1107 (1950).
8. Zuman P.: Polarographic Maxima of Second Kind, [in Czech] Chem. Listy **44**, 162 (1950).
9. Zuman P.: The Reaction of Carbonyl Compounds with Primary Amines, Proceedings 1st Internat. Polarograph. Congr., Part I (1951) [in Russian] 704; [in English] 711; Part II [in Czech] 520, Prague 1951.
10. Zuman P.: The Reaction of Pyruvic Acid with the Imidazole Derivatives, [in Czech] Chem. Listy **45**, 40 (1951).
11. Zuman P.: The Reaction of Carbonyl Compounds with Amines I. The Reaction of Pyruvic Acid with Ammonia, [in Czech] Chem. Listy **45**, 65 (1951).
12. Zuman P.: The Determination of Sulphydryl Substances in Some Fruits, [in Czech] Chem. Listy **46**, 73 (1952); [in German] Collect. Czech. Chem. Commun. **16**, 510 (1951); Proc. 1st Internat. Polarograph. Congr., Part III (1952) [in Czech] 582; [in Russian] 601; [in English] 603.
13. Zuman P.: A Contribution to the Polarography of Aluminium and Beryllium, [in Czech] Chem. Listy **46**, 326 (1952).
14. Zuman P.: Polarographic Behavior of Anthocyanines I, [in Czech] Chem. Listy **46**, 328 (1952); [in German] Collect. Czech. Chem. Commun. **18**, 36 (1953).
15. Zuman P.: Polarographic Analysis of Organic Substances, Proc. 1st Internat. Polarograph. Congr., Part III (1952) [in Czech] 146; [in Russian] 160; [in German] 177.
16. Zuman P.: The determination of Pyruvic Acid in Lactic Acid, [in Czech] Chem. Zvesti **6**, 191 (1952).
17. Koryta J., Zuman P.: The Polarography of Barbituric Acid Derivatives I. Barbituric Acid, [in Czech] Chem. Listy **46**, 389 (1952); [in German] Collect. Czech. Chem. Commun. **18**, 197 (1953).
18. Zuman P., Šantavý F.: The Polarography of Heart Glycosides Bearing an

Aldehydic Group, [in Czech] Chem. Listy **46**, 293 (1952); [in Russian] Collect. Czech. Chem. Commun. **18**, 28 (1953).

19. Valenta P., Zuman P.: A Contribution to the Polarography of Tretravelent Germanium, [in Czech] Chem. Listy **46**, 478 (1952).
20. Zuman P.: The Reaction of Carbonyl Compounds with Amines II. The Reaction of Pyruvic Acid with Glycine, Alanine and Colamine, [in Czech] Chem. Listy **46**, 512 (1952).
21. Zuman P.: The Reaction of Carbonyl Compounds with Amines III. The Reaction of the Oxidation Product of Ascorbic Acid with Ammonia, [in Czech] Chem. Listy **46**, 521 (1952).
22. Zuman P., Březina M.: The Reaction of Carbonyl Compounds with Amines IV. The Reaction of Acetone with Ammonia and Glycine, [in Czech] Chem. Listy **46**, 599 (1952).
23. Zuman P.: Aldimines, Ketimines, Schiff's Bases, [a review in Czech] Chem. Listy **46**, 688 (1952).
24. Zuman P., Procházka Z.: The Bound form of Ascorbic Acid IV. The Polarographic Determination of Ascorbic Acid in Ascorbigen Concentrates, [in Czech] Chem. Listy **47**, 357 (1953); [in Russian] Collect. Czech. Chem. Commun. **18**, 442 (1953).
25. Zuman P., Zumanová R., Souček B.: Polarographic Determination of Carbon Disulfide Using the Anodic Wave, [in Czech] Chem. Listy **47**, 178 (1953); [in German] Collect. Czech. Chem. Commun. **18**, 632 (1953).
26. Zuman P., Šantavý F.: Polarographic Study of Cyanhydrine Reaction in Alkaline Medium, [in Czech] Chem. Listy **47**, 267 (1953); [in German] Collect. Czech. Chem. Commun. **19**, 174 (1954).
27. Zuman P., Koryta J., Kalvoda R.: The Polarography of Barbituric Acid Derivaties II. Veronal, [in Czech] Chem. Listy **47**, 345 (1953); [in German] Collect. Czech. Chem. Commun. **18**, 350 (1953).
28. Březina M., Zuman P.: The Reaction of Carbonyl Compounds with Amines V. The Polarographic Study of the Reaction of Cyclanones with Primary Amines. Equilibrium State, [in Czech] Chem. Listy **47**, 975 (1953).
29. Zuman P., Tenygl J., Březina M.: The Polarography of Steroids I. Directly Reducible Ketosteroids, [in Czech] Chem. Listy **47**, 1152 (1953); [in German] Collect. Czech. Chem. Commun. **19**, 46 (1954).
30. Zuman P.: The Significance of Hammett's Equation in Polarography, [in Czech] Chem. Listy **47**, 1234 (1953); [in German] Collect. Czech. Chem. Commun. **19**, 599 (1954).
31. Zuman P., Zumanová R., Souček B.: The Polarographic Determination of Hydrogen Sulfide in the Presence of Carbon Disulfide, [in Czech] Chem. Listy **47**, 1409 (1953).
32. Zuman P., Zumanová R., Souček B.: The Polarographic Irreversibility of the

System Diethyldithiocarbamate-bis(diethylthiocarbamyl)disulfide, [in Czech] Chem. Listy **47**, 1522 (1953).

33. Zuman P.: The Polarographic Behavior of Ferrocyanide, Ferricyanide and the Prussian Blue, [in Czech] Chem. Listy **47**, 1523 (1953); [in German] Collect. Czech. Chem. Commun. **19**, 602 (1954).
34. Blatná J., Fragner J., Šanda V., Zuman P. Žuffová D.: The Determination of ℓ-Ascorbic Acid in Foods, [in Czech] Průmysl potravin **4**, 402 (1955); Czechoslovak Ministry for Food Protection, Recommended analytical methods No. 4, Prague 1953.
35. Zuman P.: Polarography in Pharmacy, [a review in Czech] Cesk. Farm. **2**, 413 (1953); [in German] Pharmazie **8**, 903 (1953).
36. Zuman P.: The Advantages of Polarographic Analysis, [in Czech] Proc. 1st Conf. Anal. Chem., 296, Prague 1953.
37. Valenta P., Zuman P.: A Note to the Article: "Polarographic Reduction of Germanium" by Das Gupta A.K., Nair C.K.N, Anal. Chim. Acta **10**, 591 (1954).
38. Zuman P.: The Influence of Structure on Polarographic Behavior of Organic Compounds, [a review in Czech] Chem. Listy **48**, 94 (1954).
39. Zuman P., Kabát M.: Polarograhic Study of Nitroprusside, [in Czech] Chem. Listy **48**, 368 (1954); [in German] Collect. Czech. Chem. Commun. **19**, 873 (1954).
40. Zuman P.: Polarograhic Behavior of Juglone and its Determination in the Presence of Ascorbic Acid in Fruits and Green Parts of the Walnut (Juglans Rregia), [in Czech] Chem. Listy **48**, 525 (1954); [in German] Collect. Czech. Chem. Commun. **19**, 1140 (1954).
41. Zumanová R., Zuman P.: The Determination of 2,3-Dimercaptopropanol (BAL) in Pharmaceutical Preparations Using Polarography and Potentiometry, [in German] Pharmazie **9**, 554 (1954).
42. Zuman P.: The Polarography of Barbituric Acid Derivatives III. Thiobarbituric Acid Derivatives, [in Czech] Chem. Listy 48, 1006 (1954); [in German] Collect. Czech. Chem. Commun. **20**, 649 (1955).
43. Zuman P.: The polarography of Barbituric Acid Derivatives IV. The Damping of Maxima by the Action of Thiobarbituric Acid Derivatives, [in Czech] Chem. Listy **48**, 1020 (1954); [in German] Collect. Czech. Chem. Commun. **20**, 883 (1955).
44. Zuman P.: The Influence of Adsorption on Polarographic Anodic Curves. The Origin of Non-Turbulent Maxima and Minima, [in Czech] Chem. Listy **48**, 1025 (1954); [in German] Collect. Czech. Chem. Commun. **20**, 876 (1955).
45. Zuman P., Zumanová R., Teisinger J.: The Polarography of Some Sulfur-Containing Compounds IV. Anodic Waves of 2,3-Dimercaptopropanol (BAL), [in Czech] Chem. Listy **48**, 1499 (1954); [in German] Collect. Czech. Chem.

Commun. **20**, 139 (1955).

46. Zuman P.: The influence of the Surface Active Substances on Polarographic Curves, [in Czech] Chem. Zvesti **8**, 789 (1954).
47. Zuman P.: The role of Hammett's Equation in the Polarographic Solution of Structural Problems, [in Czech] Chem. Zvesti **8**, 939 (1954).
48. Zuman P.: The Constitution and Polarographic Behaviour of Organic Substances, [in Czech] Chem. Zvesti **8**, 926 (1954).
49. Zuman P., Zumanová R.: The Polarography of Some Sulfur-Containing Compounds V. Compounds of2,3-Dimercaptopropanol with Heavy Metals, [in Czech] Chem. Listy **49**, 652 (1955); [in German] Collect. Czech. Chem. Commun. **21**, 123 (1956).
50. Manoušek O., Zuman P.: The Polarography of Urea and Thiourea Derivatives V. Anodic Depolarisation in the Solutions of Uracil, its Derivatives and 4-Methyl-2-thiouracil, [in Czech] Chem. Listy **49**, 668 (1955); [in German] Collect. Czech. Chem. Commun. **20**, 1340 (1955).
51. Fedoroňko M., Zuman P.: The Polarography of Some Sulfur-Containing Compounds VII. Anodic Depolarisation in the Solution of 2-Mercapto-benzthiazole and 2-Mercapto-benzimidazole, [in Czech] Chem. Listy **49**, 1484 (1955); [in German] Collect. Czech. Chem. Commun. **21**, 678 (1956).
52. Fedoroňko M., Manoušek O., Zuman P.: The Polarography of Urea and Thiourea Derivatives VII. Some Substituted Ureas, Thioureas and Isothioureas, [in Czech] Chem. Listy **49**, 1494; [in German] Collect. Czech. Chem. Commun. **21**, 672 (1956).
53. Zuman P.: Advances of Polarography in Pharmacy, [a review in Czech] Cesk. Farm. **5**, 44 (1956); [in German] Pharmazie **11**, 449 (1956).
54. Zuman P., Březina M.: The Polarography in Medicine, [a review in German] Leybold Polarogr. Ber. **3**, 224 (1955).
55. Manoušek O., Zuman P.: The Polarography of Urea and Thiourea Derivatives VIII. Polarographic Determination of Thiobarbituric Acid Derivatives and 4-Methyl-2-thiouracil in Preparations, [in Czech] Cesk. Farm. **4**, 193 (1956); [in German] Pharmazie **11**, 530 (1956).
56. Zuman P., Zumanová R.: Polarography of Some Sulfur-Containing Compounds XI. Oxidation and Certain Reactions of 2-3,-Dimercaptopropanol, [in Czech] Chem. Listy **50**, 1908 (1956); [in German] Collect. Czech. Chem. Commun. **22**, 929 (1957).
57. Zuman P., Sicher J., Krupička J., Svoboda M.: Polarographic Determination of Rate of Periodate Oxidation of Epimeric Open-Chain 1,2-Glycols, Nature **178**, 1407 (1956).
58. Zuman P., Krupička J.: Polarographic Method for the Study of Reaction of Periodic Acid with Glycols, [in Czech] Chem. Listy **51**, 424 (1957); [in English] Collect. Czech. Chem. Commun. **23**, 598 (1958).

59. Zuman P.: Polarographic Determination of Vitamins, [in German] Acta Chim. Acad. Sci. Hungary **9**, 279 (1956).
60. Zuman P.: A simple Modification of the Polarographic Vessel, [in Czech] Chem. Listy **51**, 993 (1957).
61. Zuman P., Sicher J., Krupička J., Svoboda M.: Stereochemical Studies VII. Oxidation of Diastereoisomeric Diols of the Type RCH(OH)CH(OH)R by Periodate, [in Czech] Chem. Listy **51**, 10681 (1957); [in English] Collect. Czech. Chem. Commun. **23**, 1237 (1958).
62. Zuman P.: The Role of Buffers in Analytical Chemistry, [in Czech] Chemie **9**, 192 (1957).
63. Zumanová R., Teisinger J., Zuman J.: Influence of Proteins on the Polarographic Behaviour of Metals and their Compounds with 2,3-Dimercaptopropanol, [in Czech] Chem. Zvesti **9**, 517 (1957).
64. Zuman P.: Two Examples of Application of Polarography to Studies of Homogeneous Chemical Reactions, [in Polish] Prace Konf. Polarograf., Warszawa, 339 (1956); PWN, Warszawa 1957.
65. Zuman P., Zumanová R.: Some Reactions of 2,3-Dimercaptopropanol Studied Polarographically, [in Polish] Prace Konf. Polarograf., Warszawa, 467 (1956); PWN, Warszawa 1957.
66. Zuman P., Zumanová R.: Some Reactions of 2,3-Dimercaptopropanol (BAL) with Heavy Metal and Some Oxidizing Agents, Tetrahedron **1**, 289 (1957).
67. Zahradník R., Zuman P.: Carbamates, Thiocarbamates and Dithiocarbamates VIII. Kinetics and Mechanism of Decomposition of Dithiocarbamic Acids in Acid Solutions, Studied Polarographically, [in Czech] Chem. Listy **52**, 231 (1958); [in German] Collect. Czech. Chem. Commun. **24**, 1132 (1959).
68. Zuman P., Zahradník R.: Kinetics and Mechanism of the Decomposition of Dithiocarbamates in Acidic Solutions. A polarographic Study, [in German] Z. Phys. Chem. (Leipzig) **280**, 135 (1957).
69. Zuman P.: Polarographic Study of Biochemically Important Reactions, [in Czech] Cesk. Farm. **7**, 84 (1958).
70. Zuman P.: Steric Effects on the Catalytic Evolution of Hydrogen in Ammoniacal Solutions of Cobalt in the Presence of Threo- and Erythro-Phenyl-Cystein, [in Czech] Chem. Listy **52**, 1349 (1958); [in German] Collect. Czech. Chem. Commun. **24**, 2027 (1959).
71. Zuman P., Černý V.: Polarography of Steroids III. Polarographic Reduction of Steroids Containing an Aldehydic Group in Position 18, [in Czech] Chem. Listy **52**, 1468 (1958); [in German] Collect. Czech. Chem. Commun. **24**, 1925 (1959).
72. Zuman P.: Polarography of Some Aromatic Compounds: Sydones and Azulenes, [in German] Z. Phys. Chem. (Leipzig), Sonderheft, 243 (1958).
73. Zuman P., Kuik M.: Influence of Sulfur on Catalytic Waves in Ammoniacal

Solutions of Cobaltous Salts, [in German] Naturwiss. **45**, 541 (1958).

74. Zuman P., Fedoroňko M.: Polarographic Study of Alkaline Hydrolysis of Isothioureas, [in German] Z. Phys. Chem. (Leipzig) **209**, 376 (1958).
75. Zuman P.: Discussion to the Paper: "Polarographic Reduction of Δ^4-3-Keto-teroids in Well Buffered Media" by Kabasakalian P., McGlotten J.: J. Electrochem. Soc. **105**, 758 (1958).
76. Zuman P., Chodowski J., Potěšilová H., Šantavý F.: Polarographic Study of Acid-base Reactions of Tropylium Ions, Nature **182**, 1535 (1958).
77. Zuman P.: Steric Effects in Polarography, [in Czech] Chem. Listy **53**, 154 (1959); [in German] Acta Chem. Acad. Sci. Hungary. **18**, 141 (1959).
78. Banyai E., Zuman P.: Polarographic Behaviour of 4-Amino-4-methoxyphenylamine (Variamin Blue), [in German] Collect. Czech. Chem. Commun. **24**, 522 (1959).
79. Zuman P., Kuik M.: Catalysis of Hydrogen Evolution in the Presence of Some Sulfur Derivatives of Hydantoin and Pyrimidine, [in German] Collect. Czech. Chem. Commun. **24**, 3861 (1959).
80. Zuman P.: Polarographic Microanalysis in Reaction Kinetics, Proc. Internat. Symposium Microchem., Birmingham (1958); Pergamon Press, 294 (1960).
81. Zuman P.: Polarography and Structure of Organic Compounds, Proc. Internat. Symposium Microchem., Birmingham (1958), Pergamon Press, 299 (1960).
82. Manoušek O., Zuman P.: Polarographic Determination of Pyridoxal and Pyridoxal-5-phosphate, [in German] J. Electroanalyt. Chem. **1**, 324 (1960).
83. Zuman P.: A Study of the Effect of Structure on Polarographic Behaviour of Organic Substances in Polarographic Institute of the Czechoslovak Academy of Science, [a review in Czech] Chem. Listy **54**, 1244 (1960); [in English] J. Polarograph. Soc. **7**, 66 (1961).
84. Zuman P.: Quantitative Treatments of Substituent Effects in Polarography I. General Equation for the Relation Between Polarographic Half-Wave Potentials and the Effects of Substituents, Collect. Czech. Chem. Commun. **25**, 3225 (1960).
85. Zuman P.: Polarography of Nonbenzenoid Aromatic and Related Substances II. The Course of the Reduction of Sydnones at the Dropping Mercury Electrode, Collect. Czech. Chem. Commun. **25**, 3245 (1960).
86. Zuman P.: Polarography of Nonbenzenoid Aromatic and Related Substances III. The Course of the Reduction of N,N-Polymethylene-bis-sydnones, Collect. Czech. Chem. Commun. **25**, 3252 (1960).
87. Zuman P.: Polarography of Nonbenzenoid Aromatic and Related Substances IV. Polar Effects of Substituents in Phenyl Sydnones. An Application of Modified Hammett Equation, Collect. Czech. Chem. Commun. **25**, 3256 (1960).
88. Horn G., Zuman P.: Polarography of Urea and Thiourea Derivatives XI. A Note

on Polarography of Some Mercaptopurines, [in German] Collect. Czech. Chem. Commun. **25**, 3401 (1960).

89. Zuman P., Horák V.: Polarographic Reduction of Single Carbon-Nitrogen Bond. Advances in Polarography, Proc. 2nd Internat. Congr. Polarography, Cambridge (1959); Pergamon Press, 804 (1960).
90. Zuman P.: Influence of Substituents in Aliphatic and Heterocyclic Series. Advances in Polarography, Proc. 2nd Internat. Congr. Polarograph, Cambridge (1959); Pergamon Press, 812 (1960).
91. Zuman P.: Oscillographic and Classical Polarography, [in Czech] Chem. Zvesti **14**, 869 (1960).
92. Manoušek O., Zuman P.: Polarographic Identification of the Reactive Form in the Hydrolysis of Pyridoxal-5-phosphate, Biochem. Biophys. Acta **44**, 393 (1960).
93. Horák V., Zuman P.: Fission of Activated Carbon-Nitrogen and Carbon-Sulphur Bonds. Introductory Remarks, Collect. Czech. Chem. Commun. **26**, 173 (1961).
94. Zuman P., Horák V.: Fission of Activated Carbon-Nitrogen and Carbon-Sulphur Bonds I. Polarographic Reduction of the Single C–N Bond, Collect. Czech. Chem. Commun. **26**, 176 (1961).
95. Zuman P.: A general Equation for the Effect of Substituents of Half-Wave Potentials. Contributi teorici e sperimentali di polarografia 5, Ric. Sci. **30**, 229 (1960).
96. Zuman P.: Application of Polarography to the Study of the Structure of Organic Substances and Intermediates, [a review in Czech] Chem. Listy **55**, 261 (1961); [in German] Z. Phys. Chem. (Leipzig) **3**, 161 (1963).
97. Zuman P., Chodowski J., Šantavý F.: Polarography of Nonbenzenoid Aromatic and Related Substances VII. A Polarographic Study of the Acid-Base Properties of the Tropylium Ion, Collect. Czech. Chem. Commun. **26**, 380 (1961).
98. Zuman P., Manoušek O.: Polarographic Study of the Nonenzymatic Hydrolysis of Pyridoxal-5-phosphate, Collect. Czech. Chem. Commun. **26**, 2134 (1961).
99. Zuman P., Michl J.: Role of Keto-Enol Tautomerism in Polarographic Reduction of Some Carbonyl Compounds, Nature **192**, 655 (1961).
100. Zuman P., Voaden D.J.: Polarography of Nonbenezoid Aromatic and Related Substances VI. Polarographic and Spectrophotometric Study of Hindrance of Coplanarity in 3-Phenyl-sydnones, Tetrahedron **16**, 130 (1961).
101. Zuman P., Wawzonek S.: Trends in Organic Polarography, Progress in Polarography (P. Zuman and I.M. Kolthoff, Eds.), Interscience, Vol. 1, p. 303, New York 1962.
102. Zuman P.: Current Trends in Study of the Influence of Structure on the Polarographic Behaviour of Organic Substances, Progress in Polarography (P. Zuman and I.M. Kolthoff, Eds.), Interscience, Vol. I, p. 319, New York 1962.
103. Zuman P.: Important Factors in Classical Polarography, Progress in Polarography (P. Zuman and I.M. Kolthoff, Eds.), Interscience, Vol. II, p. 58, New

York 1962.

104. Zuman P., Březina M.: Polarographic Analysis in Pharmacy, Progress in Polarography (P. Zuman and I.M. Kolthoff, Eds.), Interscience, Vol. II, p. 687, New York 1962.

105. Zuman P., Horák V.: Fission of Activated Carbon-Nitrogen and Carbon-Sulfur Bonds II. Polarographic Reduction β-Aminoketones, Collect. Czech. Chem. Commun. **27**, 187 (1962).

106. Zuman P.: Polarography of Benzenoid Halogen Hydrocarbons and Their Derivatives, [a review in Czech] Chem. Listy **56**, 219 (1962).

107. Manoušek O., Zuman P.: Direct Polarographic Determination of Pyridoxal in the Presence of Pyridoxal-5-phosphate, Collect. Czech. Chem. Commun. **27**, 486 (1962).

108. Horák V., Michl J., Zuman P.: A Contribution to the Studies of Elimination Reactions of Mannich Bases Using Polarographic Method, Tetrahedron Letters **21**, 744 (1961).

109. Horák V., Zuman P.: Synthetic and Polarographic Studies in the 3-Tropinone Series, Tetrahedron Letters **21**, 746 (1961).

110. Zuman P.: Application of Polarography to Organic Chemistry, J. Electroanal. Chem. **3**, 157 (1962).

111. Zuman P.: Quantitative Treatments of Substituent Effects in Polarography II. Free Energy Relationship in Moncyclic Heterocyclic Series, Collect. Czech. Chem. Commun. **27**, 630 (1962).

112. Zuman P.: Quantitative Treatments of Substituent Effects in Polarography III. Substituent in Ortho-Position, Collect. Czech. Chem. Commun. **27**, 648 (1962).

113. Zuman P., Chodowski J.: Polarography of Nonbenzenoid Aromatic and Related Substances VIII. Adsorption Processes During the Electroreduction of the Tropylium Ion, Collect. Czech. Chem. Commun. **27**, 759 (1962).

114. Zuman P., Zinner H.: Polarography of Tetroses and Application of Polarography in the Study of Cleavage of 1,1-Bis-alkylsulphonyl-pentos-1-enes, [in German] Chem. Ber. **95**, 2089 (1962).

115. Zuman P.: Quantitative Treatments of Substituent Effects in Polarography IV. Linear Free Energy Relationships in Quinoid Series, Collect. Czech. Chem. Commun. **27**, 2035 (1962).

116. Zuman P.: Application of Polarography in Organic Chemistry, [in Hungarian] Magyar Kemikusok Lapja **17**, 8 (1962).

117. Zuman P.: Polarography in Functional Group Analysis, Analytical Chemistry (1962); Proc. Feigl Anniv. Symp., Birmingham, Elsevier, p. 222, Amsterdam 1963.

118. Zuman P., Tang S.: Fission of Activated Carbon-Nitrogen and Carbon-Sulphur Bonds III. Reduction of the C–S$^{(+)}$ Bond in Methyl Butyl Phenacylsulphonium Perchlorate, Collect. Czech. Chem. Commun. **28**, 829 (1963).

119. Zuman P.: Organic Polarography, Structure and Linear Free Energy Relationships, Review of Polarography (Japan) **11**, 102 (1963).
120. Tang S., Zuman P.: A New Type of Maximum on the Limiting Current of the Reduction Wave of Phenacylsulfonium Ions, Collect. Czech. Chem. Commun. **28**, 1524 (1963).
121. Zuman P.: Some Techniques in Organic Polarography, Advances in Analytical Chemistry and Instrumentation (C.N. Reilley, Ed.), Interscience-Wiley, Vol. 2, p. 219, New York 1963.
122. Zuman P.: Structure, Linear Free Energy Relationships and Polarography, [in Russian] Correlation Equations in Organic Chemistry, Tartu State University, Vol. 2, p. 3, Tartu 1964.
123. Ždanov S.I., Zuman P.: Polarography of Nonbenzenoid Aromatic and Related Compounds IX. Reduction and Hydrogen Evolution Catalysis in Solutions of N-Troponyl Amino Acids, Collect. Czech. Chem. Commun. **29**, 960 (1964).
124. Talvik A., Zuman P., Exner O.: Studies on the Inductive Effect III. The Kinetics of the Reaction of Substituted Benzoic Acids with Diphenyldiazomethane, Collect. Czech. Chem. Commun. **29**, 1266 (1964).
125. Manoušek O., Zuman P.: Polarographic Study of the Reaction of Pyridoxal with Hydroxylamine, Experienta **20**, 301 (1964).
126. Manoušek O., Zuman P.: Polarography of Pyridoxine and Some of its Derivatives, Collect. Czech. Chem. Commun. **29**, 1432 (1964).
127. Manoušek O., Zuman P.: Polarographic Reduction of 2-(2-Methyl-3-hydroxy-5-hydroxy-methyl-4-pyridyl)thiazo-lidine-4-carboxylic acid, Collect. Czech. Chem. Commun. **29**, 1718 (1964).
128. Fedoroňko M., Zuman P.: Polarography of Urea and Thiourea Derivatives XIII. Kinetics of Base Catalysed Decomposition of S-Substituted Thioureas in Alkaline Solution, Collect. Czech. Chem. Commun. **29**, 2115 (1964).
129. Čárský P., Zuman P., Horák V.: Fission of Activated Carbon-Nitrogen and Carbon-Sulfur Bonds V. Polarographic Study of Elimination of β-Morpholino Propiophenone, Collect. Czech. Chem. Commun. **29**, 3044 (1964).
130. Zuman P., Manoušek O., Horák V.: Fission of Activated Carbon-Nitrogen and Carbon-Sulphur Bonds VI. Polarographic Reduction of the $C–N^{(+)}$ Bond in α-Aminonitriles, Collect. Czech. Chem. Commun. **29**, 2906 (1964).
131. Zuman P., Čárský P.: Reaction Kinetics of a Reversible Reaction which is Coupled is Two Rapidly Established Equilibria, Z. Phys. Chem. (Leipzig) **227**, 278 (1964).
132. Zuman P., Exner O.: Oxime Derivatives VIII. Polarographic Reduction of O- and N-Substituted Oximes, Collect. Czech. Chem. Commun. **30**, 1832 (1965).
133. Čárský P., Zuman P., Horák V.: Fission of Activated Carbon-Nitrogen and Carbon-Sulfur Bonds VII. Kinetics of Ketol Formation from α, β-Unsaturated Ketones in Alkaline Media, Collect. Czech. Chem. Commun. **30**, 4316 (1965).
134. Zuman P.: Recent Trends in Organic Polarography, Proc. 3rd Internat.

Polarograph. Congress, Southhampton 1964, p. 687; MacMillan, London 1966.

135. Čárský P., Horák V., Zuman P.: Polarographic Study of the Kinetics of Elimination Reaction of β-Morpholino Propiophenone, Organic Reaction Mechanisms, Chem. Soc. Spec. Publ. **19**, 180 (1965).
136. Manoušek O., Zuman P.: The Polarographic and Electrolytic Reduction of the Cyano Group in Substituted Benzonitriles, Chemical Communs., 158 (1965).
137. Šestáková I., Zuman P., Horák V.: Fission of Activated Carbon-Nitrogen and Carbon-Sulphur Bonds VIII. Elimination of β-Piperidinoethyl Phenyl Sulphone Methoidide and Reaction of Phenyl Vinyl Sulphone with Hydroxyl Ions, Collect. Czech. Chem. Commun. **31**, 827 (1966).
138. Kucharczyk N., Adamovský M., Horák V., Zuman P.: Slowly Established Acid-Base Equilibrium in Organic Polarography: Tautometric Changes Between 3-Thianaphthenone and 3-Hydroxy Thianaphthene, J. Electroanal. Chem. **10**, 503 (1965).
139. Zuman P.: Polarography of Alicyclic Compounds, Talanta **12**, 1337 (1965).
140. Zuman P.: Application of Polarography in Organic Analysis and in the Solution of Some Fundamental Problems of Organic Chemistry, [in German] Z. Anal. Chem. **216**, 151 (1966).
141. Fleet B., Zuman P.: Quantitative Treatment of Substituent Effects in Polarography V. Polarographic Reduction of Some Semicarbazones, Collect. Czech. Chem. Commun. **32**, 2066 (1967).
142. Suchomelová L., Zýka L., Zuman P.: Effects of Structure of the Alkyl Group on the Polarographic Waves Corresponding to Catalytic Hydrogen Evolution by Organic Sulphoxides, J. Electroanal. Chem. **12**, 194 (1966).
143. Zuman P.: Oxidation of Chromic Oxide. Complete Kinetic Treatment of the Oxidation of Secondary Alcohols, Collect. Czech. Chem. Commun. **32**, 1610 (1967).
144. Kargin J., Manoušek O., Zuman P.: Polarographic Behaviour of *p*-Diacetylbenzene. An Example of a Compound with Two Electroactive Centres, J. Electroanal. Chem. **12**, 443 (1966).
145. Zuman P.: Polarographic Behaviour of Organic Substances Bearing Two Electronegative Groups, [in German] Z. Anal. Chem. **224**, 374 (1967).
146. Šestáková, I., Horák V., Zuman P.: Fission of Activated Carbon-Nitrogen and Carbon-Sulphur Bonds IX. Polarographic Study of Addition of Primary Amines to Phenyl Vinyl Ketone, Collect. Czech. Chem. Commun. **31**, 3889 (1966).
147. Zuman P.: Physical Organic Polarography (A. Streitwiesser, Jr. and R.W. Taft, Eds.), Progr. Physical Org. Chem. **5**, 81 (1967).
148. Zuman P.: Polarography and Reaction Kinetics (R. Gold, Ed.), Adv. Physical Org. Chem. **5**, 1 (1967).
149. Janata J., Schmidt O., Zuman P.: Application of Analogue Computers to the

Studies of Reactions Involving Electrolytically Generated Reagent II. Treatment of Consecutive and Competitive Reactions, Collect. Czech. Chem. Commun. **31**, 2344 (1966).

150. Bashar A., Townshend A., Zuman P.: Polarographic Evidence for the Structure of the So-Called Phenylthiohydantoic Acid, Collect. Czech. Chem. Commun., **32**, 901 (1967).
151. Zuman P., Barnes D.: Desorption of 3-Phenylpropionaldehyde Preceding Polarographic Reduction, Nature **215**, 1269 (1967).
152. Zuman P.: Preparative Methods Used in the Elucidation of Organic Electrode Processes, J. Polarograph. Soc. **13**, 53 (1967).
153. Zuman P.: Some Applications of Polarography in Organic Chemistry, Mises au Point de Chim. Anal. Org. Pharm. Bromatol. **17**, 219 (1968).
154. Barnes D., Belcher R., Zuman P.: The Use of Submicroanalysis and Flame Ionization Detecting Gas-Liquid Chromatograph in the Identification of Electroysis Products at the Dropping Mercury Electrode, Talanta **14**, 1197 (1967).
155. Hall D.J., Townshend A., Zuman P.: Polarography of Some Sulphur-Containing Compounds XII. Anodic Waves of Monoalkyldithiocarbamates and their Reaction with Heavy Metals, Anal. Chem. Acta **40**, 459 (1968).
156. Halls D.J., Townshend A., Zuman P.: Polarography of Some Sulphur-Containing Compounds XIII. Anodic Waves of Dialkyldithiocarbamates, Anal. Chim. Acta **41**, 51 (1968).
157. Halls D.J., Townshend A., Zuman P.: Polarography of Some Sulphur-Containing Compounds XIV. Anodic Waves of Ethylene-bis-dithiocarbamates and their Reactions with Heavy Metals, Anal. Chim. Acta **41**, 63 (1968).
158. Barnes D., Zuman P.: Polarographic Reduction of Cinnamaldehyde; Comparison with 3-Phenyl-propionaldehyde and Phenylpropargylaldehyde, J. Electroanal. Chem. **16**, 575 (1968).
159. Manoušek O., Exner O., Zuman P.: Fission of Activated Carbon-Nitrogen and Carbon-Sulfur Bonds X. Polarographic Reduction of Substituted Methyl Phenyl Sulphones, Collect. Czech. Chem. Commun. **33**, 3988 (1968).
160. Manoušek O., Exner O., Zuman P.: Fission of Activated Carbon-Nitrogen and Carbon-Sulfur Bonds XI. Polarographic Reduction of Substituted Benzene Sulphonamides, Collect. Czech. Chem. Commun. **33**, 4000 (1968).
161. Zuman P.: Polarographic Reduction of Aldehydes and Ketones I. Course of the Electrode Process, Collect. Czech. Chem. Commun. **33**, 2548 (1968).
162. Zuman P., Turcsanyi B.: Polarographic Reduction of Aldehydes and Ketones II. pH-Dependence of Polarographic Limiting Currents of Aryl Alkyl Ketones Governed by the Rate of Simultaneous Reactions with Several Acids Producing the Electroactive Species, Collect. Czech. Chem. Commun. **33**, 3090 (1968).

163. Zuman P., Turcsanyi B.: Polarographic Reduction of Aldehydes and Ketones IV. Linear Free Energy Treatment of Substituted Benzophones, Collect. Czech. Chem. Commun. **33**, 323 (1968).
164. Zuman P., Exner O., Rekker R.F., Nauta W.Th.: Polarographic Reduction of Aldehydes and Ketones IV. Linear Free Energy Treatment of Substituted Benzophenones, Collect. Czech. Chem. Commun. **33**, 323 (1968).
165. Šestáková I., Pecka J., Zuman P.: Polarographic Reduction of Aldehydes and Ketones V. β-Ketosulphides, Collect. Czech. Chem. Commun. **33**, 3227 (1968).
166. Zuman P.: Polarographic Methods, Fast Reactions in Enzymology (K. Kustin, Ed.), p. 121, Academic Press, New York 1969.
167. Halls D.J., Townshend A., Zuman P.: Polarographic Determination of Some Dithiocarbamates and their Heavy Metal Complexes, Analyst **93**, 219 (1968).
168. P. Zuman P., Barnes D., Ryvolová-Kejharová A.: Polarographic Reduction of Some Carbonyl Compounds, Disc. Faraday Soc. **45**, 202 (1968).
169. Barnes D., Zuman P.: Polarographic Determination of Caesium in the Presence of Other Alkali Metals Based on Interaction with the Cinnamaldehyde Radical Anion, Analyst **93**, 589 (1968).
170. Zuman P., Manoušek O., Vig S.K.: Further Examples of Para- and Ortho-Disubstituted Benzene Derivatives Reduced in a Reversible Two-Electron Step into Products of Limited Stability, J. Electroanal. Chem. **19**, 147 (1968).
171. Manoušek O., Zuman P., Exner O.: Quantitative Treatment of Substituent Effects in Polarography VI. Polarographic Reduction of Benzonitriles *m*- and *p*-Substituted with Electronegative Groups, Collect. Czech. Chem. Commun. **33**, 3979 (1968).
172. Zuman P., Manoušek O.: Fission of Activated Carbon-Nitrogen and Carbon-Sulphur Bonds XII. Polarographic Reduction of Substituted Benzonitriles Bearing in Para-Positon a Carbonyl Group in Acidic Media, Collect. Czech. Chem. Commun. **34**, 1580 (1969).
173. Čárský P., Zuman P.: The Use of a Simple Molecular Orbital Theory to Elucidate the Polarographic Behaviour of Some Para-Substituted Benzonitriles, Collect. Czech. Chem. Commun. **34**, 497 (1969).
174. Zuman P., Ryvolová-Kejharová A.: Desorption Preceding Polarographic Reduction of Some Acetophenone Derivatives in Alkaline Media, Anal. Letters **1**, 429 (1968).
175. Kakáč B., Mňouček K., Zuman P., Semonský M., Zikán V., Černý A.: Substances with Antineoplastic Activity XXII. Spectral and Polarographic Properties of β-4-Methoxy-benzoyl-β-bromo and β-Chloroacrylic Acids and Related Compounds, Collect. Czech. Chem. Commun. **33**, 1256 (1968).
176. Zuman P.: Polarography in Organic Chemistry, Fortschr. Chem. Forschg. **12**, 1 (1969).
177. Barnes D., Zuman P.: Polarographic Reduction of Aldehydes and Ketones,

Part 6. Behaviour of Cinnamaldehyde at Lower pH Values, Trans. Faraday Soc. **65**, 1668 (1969).

178. Barnes D., Zuman P.: Polarographic Reduction of Aldehydes and Ketones, Part 7. Cinnamaldehyde at Higher pH-Values, Trans. Faraday Soc. **65**, 1681 (1969).
179. Zuman P.: Polarography of Biomolecules. Experimental Methods in Biophysical Chemistry (C. Nicolau, Ed.), p. 393, J. Wiley, New York 1973.
180. Ryvolová-Kejharová A., Zuman P.: Polarographic Reduction of Aldehydes and Ketones VIII. Polarographic Behaviour of Chalcone and Dihydrochalcone, J. Electroanal. Chem. **21**, 197 (1969).
181. Barnes D., Zuman P.: Effect of pH on Concentration of Species Present in Aqueous Solutions of Carbonyl Compounds Affected by Hydration-Dehydration and Keto-Enol Equilibria, Talanta **16**, 975 (1969).
182. Nişli G., Barnes D., Zuman P.: Polarographic Reduction of Aldehydes and Ketones IX. Carbanion Formation which Accompanies the Electro-Reduction of Ethyl Benzoylacetate, J. Chem. Soc. **(B)**, 764 (1970).
183. Nişli G., BarnesD., Zuman P.: Polarographic Reduction of Aldehydes and Ketones X. Recombination of Carbanions of ω-Cyanoacetophenone, J. Chem. Soc. **(B)**, 771 (1970).
184. Nişli G., Barnes D., Zuman P.: Polarographic Reduction of Aldehydes and Ketones XI. Acid-Base Equilibria Accompanying Electrolysis of 1-Phenyl-1,3-butanedione, J. Chem. Soc. **(B)**, 778 (1970).
185. Ryvolová-Kejharová A., Zuman P.: Polarographic Reduction of Aldehydes and Ketones XII. Simultaneous Reduction of Two Carbonyl Groups in 4,4'-Diacetyldiphenyl-methane, Collect. Czech. Chem. Commun. **35**, 22 (1970).
186. Barnes D., Uden P.C., Zuman P.: Polarographic Reduction of Aldehydes and Ketones XIII. Effect of Hydration and Carbanion-Enolate Formation on the Electrolysis of Glycolaldehyde, J. Chem. Soc. **(B)**, 1114 (1971).
187. Barnes D., Zuman P.: Polarographic Reduction of Aldehydes and Ketones XIV. Formation of Trans- and Cis-Crotylalcohol in the Electroreduction of Crotonaldehyde, J. Chem. Soc. **(B)**, 1118 (1971).
188. Barnes D., Uden P.C., Zuman P.: Gas-Liquid Chromatographic Analysis of Mixtures of Cis- and Trans-Crotylalcohols in Commercial Samples and Products of Controlled Potential Electrolysis, Anal. Letters **3**, 633 (1970).
189. Smyth W.F., Svehla G., Zuman P.: Polarography of Some Sulphur Containing Compounds XV. Polarographic and Spectral Investigations of Acid-Base Equilibria in Aqueous Solutions of Substituted 2-Thiobarbiturates, Anal. Chim. Acta **51**, 463 (1970).
190. Smyth W.F., Svehla G., Zuman P.: Polarography of Some Sulphur-Containing Compounds XVI. Polarographic and Spectral Investigation of Acid-Base Equilibria in Aqueous Solutions of 2-Thiobarbituric Acids Bearing Alkyl

Groups on Sulphur, Anal. Chim. Acta **52**, 129 (1970).

191. Smyth W.F., Zuman P., Svehla G.: Polarography of Some Sulphur Containing Compounds XVII. Polarographic and Spectral Investigation of Some Amino and Imino Derivatives of 2-Thiobarbituric Acid, J. Electroanal. Chem. **30**, 101 (1971).
192. Zuman P.: Effects of Acidity in the Elucidation of Organic Electrode Processes (P. Zuman, L. Meites, and I.M. Kolthoff, Eds), Progress in Polarography **3**, 73 (1972).
193. Ryvolová-Kejharová A., Zuman P.: Polarographic Reduction of Aldehydes and Ketones XVI. Ionization of Phthalimide, Collect. Czech. Chem. Commun. **36**, 1019 (1971).
194. Hojman J., Stefanović A., Stanković B., Zuman P.: Polarographic Reduction of Rubeanic Acid and the Catalytic Waves Observed in the Presence of Ruthenium Trichloride, J. Electroanal. Chem. **30**, 469 (1971).
195. Bover W.J., Zuman P.: J_Acidity Scale Based on Addition of Hydroxyl Ions to Substituted Benzaldehydes, J. Am. Chem. Soc. **95**, 2531 (1973).
196. Bover W.J., Zuman P.: Lewis Acid Properties of Benzaldehydes and Substituent Effects, J. Chem. Soc., Perkins Trans. II, 786 (1973).
197. Barnes D., Zuman P.: Polarographic Reduction of Aldehydes and Ketones XV. Hydration and Acid-Base Equilibria Accompanying Reduction of Aliphatic Aldehydes, J. Electroanal. Chem. **46**, 323 (1973).
198. Barnes D., Zuman P.: Polarographic Reduction of Aldehydes and Ketones XVII. Hydration and Carbanion-Enolate Formation Accompanying Reduction of Phenylacetaldehydes, J. Electroanal. Chem. **46**, 343 (1973).
199. Zuman P.: Relation Between Micro and Macro Phenomena, Organic Electrochemistry (M. Baizer, Ed.), p. 155, M. Dekker, New York 1973.
200. Zuman P.: Polarography in the Study of Some Analytically Important Reactions, Proc. Soc. Analyt. Chem. **11**, 338 (1974).
201. Bover W.J., Zuman P.: Electrooxidation of Organic Compounds I. Oxidation of Benzaldehydes at the Dropping Mercury Electrode, J. Electrochem. Soc. **122**, 368 (1975).
202. Singer S., Zuman P.: Polarographic and Spectrophotometric Determination of Acid Dissociation Constants of Some Substituted Ethyl Benzoylbenzoates, J. Org. Chem. **39**, 836 (1974).
203. Deshler L., Zuman P.: Polarographic Reduction of Aldehydes and Ketones XVIII, Ethacrynic Acid, Anal. Chim. Acta **73**, 337 (1974).
204. Romer M.M., Zuman P.: Polarographic Reduction of Haloacetones: Differences and Similarities, J. Electroanal. Chem. **64**, 258 (1975).
205. Toure V., Levy M., Zuman P.: Polarographic Reduction of Aldehydes and Ketones XX. Electro-Reduction of Cyclenones, J. Electroanal. Chem. **56**, 295 (1974).
206. Zuman P., Spritzer L.: Difference in Products of Electro-Reduction of Some

α,β-Unsaturated Aldehydes and Ketones, J. Electroanal. Chem. **69**, 433 (1976).

207. Pouw Th.J.M., Zuman P.: A J_Acidity Function for Solutions of Sodium Hydroxide in Water/Ethanol and Water/Dimethylsulfoxide Mixtures, J. Org. Chem. **41**, 1641 (1976).
208. Pouw Th.J.M., Bover W.J., Zuman P.: Acidity Functions in Solutions of Strong Bases in Mixed Solvents (W.F. Furter, Ed.), Advances in Chemistry, Thermodynamic Behavior of Electrolytes in Mixed Solvents **155**, 343 (1976).
209. Scott W.J., Zuman P.: Hydration-Dehydration Constants of α,α,α-Trifluoroacetophenone by Spectral and Electrochemical Methods, J. Chem. Soc., Faraday Trans. I **72**, 1192 (1976).
210. Matijević E., Poskanzer A.M., Zuman P.: The Characterization of the Stannous Chloride Palladium Chloride Catalyst for Electroless Plating, Plating and Surface Finishing, 958 (1975).
211. Zuman P.: Polarography in Attacking Practical and Theoretical Problems in Analytical Chemistry, Proc. Anal. Division Chem. Soc. **12**, 199 (1975).
212. Szafranski W.A., Zuman P.: Difference Between Polarographic Reduction of Chloral and Bromal, J. Electroanal. Chem. **64**, 255 (1975).
213. Zuman P., Pouw Th.J.M.: The Use of Selectrode as a Catalytically Active Electrode in Recording Current-Voltage Curves, J. Electroanal. Chem. **67**, 387 (1976).
214. Kuder J., Wychick D., Zuman P.: Polarographic Reduction of Benzylidene-Malononitrile, J. Electroanal. Chem. **71**, 297 (1976).
215. Scott W.J., Bover W.J., Bratin K., Zuman P.: Nucleophilic Additions to Aldehydes and Ketones II. Reactions of Heterocyclic Aldehydes with Hydroxide Ions, J. Org. Chem. **41**, 1952 (1976).
216. Sedon J.H., Zuman P.: Nucleophilic Additions to Aldehydes and Ketones III. Reactions of Ortho Substituted Benzaldehydes and their Polarographic Oxidations, J. Org. Chem. **41**, 1957 (1976).
217. Barnes D., Zuman P.: Effect of Oxygen on Aldolization Reactions, Nature **257**, 303 (1975).
218. Zuman P.: Techniques, Advantages and Limitations of Organic Electroanalytical Procedures in Nonaqueous media, Electrochimica Acta **21**, 687 (1976).
219. Szyper M., Zuman P.: Electronic Absorption of Carboxylic Acids and their Anions, Anal. Chim. Acta **85**, 357 (1976).
220. Cooper R.G., Zuman P.: Polarographic Reduction of 1,5-Diazo-4,8-dihydroxy-10-*n*-butyl Phenanthrene 2,6-Dicarboxylic Acid (ICI 74, 197); Simultaneous Reduction of Two Electroactive Centers, Electrochimica Acta **22**, 105 (1977).
221. Zuman P.: Effect of Hydration on Polarographic Reduction of Some Carbonyl Compounds, J. Electroanal. Chem. **75**, 523 (1977).

222. Zuman P.: Polarography, Chapter 37 in Systematic Materials Analysis, (J.H. Richardson and R.V. Peterson, Eds), Vol. IV, p. 225, Academic Press, New York.
223. Zuman P., Vida J.A., Kardos A., Romer M.: Determination of p*K*-Values of Some Barbituric Acid Derivatives, Anal. Letters **9**, 849 (1976).
224. Szafranski W., Zuman P.: Electronic Absorption of Hydroxide Ions, Anal. Chim. Acta **87**, 209 (1976).
225. Romer M., Donaruma L.G., Zuman P.: Spectrophotometric and Polarographic Analysis of Phenobarbital, N-Methylphenobarbital and N-Methoxymethylphenobarbital in a Mixture, Anal. Chim. Acta **88**, 261 (1977).
226. Zuman P., Szafranski W.: Ultraviolet Spectra of Hydroxide, Alkoxide, and Hydrogen Sulfide Anions, Anal. Chem. **48**, 2162 (1976).
227. Meites L., Zuman P.: A Comprehensive Critical Collect. Czech. Chem. Commun. of Electrochemical Data, Proceedings of Fifth Biennial Internat. Codata Conf., 593 (1977).
228. Meites L., Nürnberg H., Zuman P.: Classification and Nomenclature of Electroanalytical Techniques, Pure and Appl. Chem. **45**, 81 (1976).
229. Zuman P., Szyper M.: Polarography and Solvatochromism I. Polarographic Reduction of 5'-Methoxy-2'-hydroxy-N-methyl-4-stilbazolium Iodide and Related Compounds, J. Chem. Soc., Faraday Trans. I **73**, 1017 (1977).
230. Szyper M., Zuman P., Gibson H.W.: Polarography and Solvatochromism II. Comparison of Electrochemical and Spectral Properties of 5'-Methoxy-2'-hydroxy-N- methyl-stilbazolium Iodide, J. Chem. Soc., Faraday Trans. I **73**, 1032 (1977).
231. Meites L., Campbell B.H., Zuman P.: Development and Publication of New Polarographic and Related Methods of Analysis, Talanta **24**, 709 (1977).
232. Zuman P., Wawzonek S.: Nonaqueous Solvents in Organic Electroanalytical Chemistry, (J.J. Lagowski, Ed.), The Chemistry of Nonaqueous Solvents, Vol. 5A, p. 121, 1978.
233. Zuman P.: Polarographic Methods for Use in Biological Systems, Proc. Anal. Div. Chem. Soc. **14**, 320 (1977).
234. Rubio M.A., Pethica B.A., Zuman P., Falkenhag S.I.: The Interactions of Carcinogens and Co-Carcinogens with Lignin and Other Components of Dietary Fiber, Dietary Fibers and Nutrition (G.E. Inglett and S.I. Falkehag, Eds), Academic Press, p. 251, New York 1979.
235. Patriarche G.J., Chateau-Gosselin M., Vandenbalck J.L., Zuman P.: Polarography and Related Electroanalytical Techniques in Pharmacy and Pharmacology (A.J. Bard, Ed.), Electroanal. Chem. **11**, 141 (1979).
236. Rosenthal D., Zuman P.: Acid-Base Equilibria, Buffers, and Titrations in Water, Treatise on Anal. Chem. (I.M. Kolthoff and P.J. Elving, Eds), Part I, Vol. 2, 2nd Ed., p. 157, J. Wiley and Sons, New York 1979.
237. Dejardin-Duchene M., Patriarche G.J., Lapiere G.L., Zuman P.: Polarographic

Reduction of Aldehydes and Ketones XXI. 4-Methoxy and 4-Hydroxy-5-azacoumarine, J. Electroanal. Chem. **114**, 247 (1980).

238. DeBoer H.S., Zuman P., van Oort W.J.: Polarographic Analysis for Corticosteroids, Part 5. Reduction Mechanism of Halogenatom Containing Cortisosteroids and Analysis of Some Preparations, Anal. Chim. Acta **120**, 31 (1980).
239. Rusling J.F., Zuman P.: Effect of Buffers on Polarographic Reduction of Pyridine- Carboxaldehydes, Anal. Chem. **52**, 2209 (1980).
240. Segretario J., Rusling J.F., Zuman P.: Acidity Functions for Treatment of Polarographic Reductions of Carbonyl Compounds Involving Acid Catalyzed Dehydration, J. Electroanal. Chem. **117**, 341 (1981).
241. Meites L., Zuman P., Rupp E., Narayanan A.: Recent Developments in the Collect. Czech. Chem. Commun., Critical Evaluation, and Publication of Polarographic and Related Data, Proc. 7th Internat. Codata Conf., 418 (1981).
242. Rusling J.F., Zuman P.: Stereospecificity in the Reductive Coupling of 4-Pyridine- Carboxaldehydes, J. Org. Chem. **46**, 1906 (1981).
243. Scott W.J., Zuman P.: Polarographic Reduction of Aldehydes and Ketones, Part 19. Hydration-Dehydration Equilibria and Their Effect on Reduction of α,α,α-tTifluoro-acetophenone, Anal. Chim. Acta **126**, 71 (1981).
244. Scott W.J., Zuman P.: Reaction of α,α,α-Trifluoroacetophenone with Ammonia, Anal. Chim. Acta **126**, 259 (1981).
245. DeBoer H.S., van Oort W.J., Zuman P.: Polarographic Analysis of Corticosteroids, Part 6. Mechanism of Polarographic Reduction of Some Δ^4-3-Ketosteroids and $\Delta^{1,4}$-3-Ketosteroids, Anal. Chim. Acta **130**, 111 (1981).
246. Spritzer L., Zuman P.: Polarographic Reduction of Aldehydes and Ketones XXII. Reduction and Oxidation of α,β-Unsaturated Aldehydes: Acrolein, Tigladehyde and Substituted Cinnamaldehydes, J. Electroanal. Chem. **126**, 21 (1981).
247. DeBoer H.S., van Oort W.J., Zuman P.: Anal. Chem. Symposia Series 10, (S. Görög, Ed.), Proc. Symposium on the Analysis of Steroids, Eger, Hungary (1981); Polarography of Corticosteroids (The Reduction Mechanism), p. 535, Elsevier, Amsterdam 1982.
248. van Oort W.J., DeBoer H.S., Zuman P.: Anal. Chem. Symposia Series 10 (S. Görög, Ed.), Proc. Symposium on the Analysis of Steriods, Eger, Hungary (1981); Polarography of Corticosteroids, (Essay for Pharmaceutical Preparations), p. 541, Elsevier, Amsterdam 1982.
249. Rusling J.F., Zuman P.: A Novel Type of Effect of an Acid-Base Equilibrium Preceding Electroreduction: Polarographic Reduction of the Conjugate Base of a Non-Reducible Ecid, J. Electroanal. Chem. **143**, 283 (1983).
250. Fleury M.B., Tohier J., Zuman P.: Competitive Reduction of the Carbonyl Group and of the C–S Bond in 3-Thio-2-oxoalkanoic Acids and their Deriva-

tives at the Dropping Mercury and Mercury Pool Electrodes, J. Electroanal. Chem. **143**, 253 (1983).

251. Rusling J.F., Segretario J.P., Zuman P.: Polarographic Reduction of Aldehydes and Ketones XXIII. Electroreduction of 1-Methylpyridiniumcarboxaldehydes, J. Electroanal. Chem. **143**, 291 (1983).
252. Zutshi K., Ryschkewitsch G.E., Zuman P.: Structural Effects on Polarographic Reduction of Substituted Trimethylamine-N-pyridylboronium Cations in Acetonitrile, Inorg. Chem. **22**, 564 (1983).
253. Jandík P., Zuman P., Meites L.: Comparison of Activity of Hydroxide and Alkoxide Ions Based on Acidity Functions, J. Chem. Soc., Faraday Trans. **79**, 721 (1983).
254. Zuman P.: Relation Between Micro and Macro Phenomena, in 'Organic Electrochemistry' (M.M. Baizer and H. Lund, Eds), 2nd ed., p. 151, M. Dekker, New York 1983.
255. Zuman P.: Reporting of Organic Electrochemical Data, in 'Organic Electrochemistry' (M.M. Baizer and H. Lund, Eds), 2nd ed., p. 1055, M. Dekker, New York 1983.
256. Meites L., Zuman P.: A Comprehensive Critical Collect. Czech. Chem. Commun. of Electrochemical Data, Trends in Anal. Chem. **2**, 95 (1983).
257. Paden C.A., Frank A.S., Wieber J.M., Pethica B.A., Zuman P., Jurasek L.: Properties of Wood Lignin, ACS Symposium Series **214**, 241 (1983).
258. Frank A.S., Zuman P.: Acid-Base and Photochemical Reactions of Selenious Acid, Anal. Letters **15**(A20), 1609 (1982).
259. Jandík P., Meites L., Zuman P.: Calorimetric and Spectrophotometric Determination of the Dissociation Constant of Ethanol in Dilute Aqueous Solutions, J. Phys. Chem. **87**, 238 (1983).
260. Segretario J.P., Meites L., Zuman P.: Studies in the Theory of the Polarographic Diffusion Current VIII. The Temperature Coefficients of Ionic Conductances and Polarographic Diffusion Currents, J. Electroanal. Chem. **151**, 11 (1983).
261. van Oort W.J., Sorel R.H.A., Brusee D., Schulman S.G., Zuman P., Den Hartigh J.: Polarographic Reduction and Determination of Nalixidic Acid, Anal. Chim. Acta **149**, 175 (1983).
262. Zuman P.: Mutual Interactions Between Electrochemistry, Organic Chemistry and Biological Sciences, J. Electroanal. Chem. **168**, 249 (1984).
263. Holthuis J.J.M., van Oort W.J., Romkens F.M.G.M., Renema J., Zuman P.: Electrochemistry of Podophyllotoxin Derivatives, Part I. Oxidation Mechanism of Etoposide, J. Electroanal. Chem. **184**, 317 (1985).
264. Zuman P., Rupp E., Meites L.: Selecting Data Obtained by Electroanalytical Methods and their Correlations Using Extra Thermodynamic Treatments, "The Role of Data in Scientific Progress" (P.S. Glaeser, Ed.), p. 341, Elsevier Science Publ. B.V., Amsterdam 1985.

265. Meites L., Zuman P., Nürnberg H.W.: Recommended Terms, Symbols, and Definitions for Electroanalytical Chemistry (Recommendations 1985), Pure Appl. Chem. **57**, 1491 (1985).

266. Rusling J.F., Zuman P.: Polarographic Reduction of Aldehydes and Ketones. Part XXIV. Electroreduction of Pyridine Carboxaldehydes in Acidic Solutions, J. Electroanal. Chem. **213**, 245 (1986).

267. Rusling J.F., Zuman P.: Polarographic Reduction of Aldehydes and Ketones. Part XXV. Electroreduction of Pyridine Carboxaldehydes in Aqueous Buffered Solutions, J. Electroanal. Chem. **213**, 255 (1986).

268. Rusling J.F., Zuman P.: Polarographic Reduction of Aldehydes and Ketones. Part XXVI. Electroreduction and Electrooxidation of Pyridine Carboxaldehydes in Alkaline Solutions, J. Electroanal. Chem. **213**, 277 (1986).

269. Segretario J.P., Zuman P.: Polarographic Reduction of Aldehydes and Ketones. Part XXVII. 1-Phenyl-1,2-propanedione, J. Electroanal. Chem. **214**, 237 (1986).

270. Segretario J.P., Sleszynski N., Zuman P.: Polarographic Reduction of Aldehydes and Ketones. Part XXVIII. 1,2-Cydohexanedione, J. Electroanal. Chem. **214**, 259 (1986).

271. Kulik F., Wieber J., Pethica B., Zuman P.: Binding of Copper(II) and Zinc(II) Ions on Various Lignins, J. Electroanal. Chem. **214**, 331 (1986).

272. Segretario J.P., Sleszynski N., Partch R.E., Zuman P., Horak V.: Structural Effects Affecting Hydration of 1,2-Diones Studied by Linear Sweep Voltammetry, J. Org. Chem. **51**, 5393 (1986).

273. Holthuis J.J.M., Vendrig D.E.M.M., van Oort W.J., Zuman P.: Electrochemistry of Podophyllotoxin Derivatives. Part II. Oxidation of Teniposide and Some Epipodophyllotoxin Derivatives, J. Electroanal. Chem. **220**, 101 (1987).

274. Almstead N., Christ W., Miller G., Reilly-Packard S., Vargas K., Zuman P.: Equilibria in Solution of Methanol or Ethanol, Sulfuric Acid, and Alkyl Sulfates, Tetrahedron Letters **28**, 1627-1628 (1987).

275. DegelF., Zuman P., Jandík P., Gilch G.: Effect of Pretreating Samples with Boric Acid before Liquid Chromatography Determination of Primary Catecholamines, Clin. Chem. **33**, 106 (1987).

276. Sleszynski N., Zuman P.: Enol Form of 2,3-Butadione (Biacetyl), J. Org. Chem. **52**, 2622 (1987).

277. Kozlowski J., Zuman P.: Polarographic Reduction of Aldehydes and Ketones. Part XXX. Effects of Acid-Base, Hydration-Dehydration and Keto-Enol Equilibria on Reduction of α-Ketoglutoric and Oxalacetic Acid and Their Esters, J. Electroanal. Chem. **226**, 69 (1987).

278. Zuman P.: Electroanalytical and Optical Methods in the Study of Analytically Important Reactions, Microchem. J. **36**, 54 (1987).

279. Zuman P., German C.: Reaction of Pyruvate Anions with Alkali Metal

Cations, Naturwiss. **74**, 347 (1987).

280. Zuman P.: Electrolyses of Organic Compounds with Microelectrodes with Renewable Surfaces: Comparison of Dropping Mercury and Mercury Pool Electrodes, Microchem. J. **36**, 255 (1987).
281. Rusling J.F., Zuman P.: Reversible Formation of a Pseudobase from 1-Methylpyridinium-3-carb(ox)aldehyde, Heterocycles **26**, 3071 (1987).
282. Chatten L.G., Moskalyk R.E., Chin A., Zuman P.: A Study of the Polarographic Reduction of Methaqualone, Anal. Chim. Acta **200**, 281 (1987).
283. Bond A.M., Dakternieks D., Deprez P.P., Zuman P.: Polarographic and Spectroscopic Examination of the Reaction of the Anabolic Steroid Oxymetholone with Methanol and Ethanol, J. Org. Chem. **53**, 1991 (1988).
284. Zuman P., Rupp E.: Electrochemical Data — Do You Need Them?, Piecing the Puzzle Together, Proceedings (L.J. Alison and R.J. Olson, Eds), National Governors Assoc., p. 261, Washington, DC 1988.
285. Zuman P., German C.: Ion-Pair Formation in Aqueous Solutions of Pyruvate Anions. Polarographic Study, Bioelectr. Bioenerg. **19**, 29 (1988).
286. Zuman P., Holthuis J.J.M.: Mechanism of Electrooxidation of Substituted Phenols in Aqueous Solutions: Some Podophyllotoxin Derivatives as Models, Rec. Trav. Chim. Pays-Bas **107**, 403 (1988).
287. Zuman P., Ainso S., Paden C., Pethica B.A.: Sorptions on Lignin, Wood and Celluloses. I. Bile Salts, Colloids Surf. **33**, 121 (1988).
288. Ainso S., Paden C., Pethica B.A., Zuman P.: Sorptions on Lignin, Wood and Celluloses. II. Nitrosamines, Colloids Surf. **33**, 133 (1988).
289. Wieber J., Kulik F., Pethica B.A., Zuman P.: Sorptions on Lignin, Wood and Celluloses. III. Copper(II) and Zinc(II) Ions, Colloids Surf. **33**, 141 (1988).
290. Milberg C., Kratohvil J.P., Zuman P.: Surface Orientation of Cholanoic Acids from Suppression of Polarographic Maxima, J. Colloid Interface Sci. **126**, 63 (1988).
291. Kozlowski J., Zuman P.: Studies on Acid-Base Hydration-Dehydration and Keto-Enol Equilibria in Aqueous Solutions of α-Ketoacids by Polarography, Linear Sweep Voltammetry and Spectroscopy in Redox Chemistry and Interfacial Behavior of Biological Molecules (G. Dryhurst and K. Niki, Eds), p. 333, Plenum Press, New York. 1988.
292. Zuman P.: With the Drop of Mercury to the Nobel Prize in "Electrochemistry, Past and Present" (J.T. Stock and M.V. Orna, Eds), American Chemical Society Symposium Series 390, p. 339, American Chemical Society, Washington, DC 1989.
293. Svoronos P., Horák V., Zuman P.: Polarographic Study of Structure-Properties Relationship of *p*-Tosyl Sulfilimines, Phosphorus, Sulfur and Silicon **42**, 139 (1989).
294. Fijalek Z., Zuman P.: Determination of Methimazole and Carbimazole Using Polarography and Voltammetry, Anal. Letters **23**, 1213 (1990).

295. Zuman P., Fijalek Z.: Polarographic and Spectrophotometric Study of the Base Catalyzed Hydrolysis of Carbimazole, Anal. Letters **23**, 1201 (1990).
296. Zuman P., Fijalek Z.: Contribution to the Understanding of the Reduction Mechanism of Nitrobenzene, J. Electroanal. Chem. **296**, 583 (1990).
297. Zuman P., Fijalek Z.: Reaction of Electrogenerated Arylhydroxylamines and Nitroso-Benzene in the Course of the Reduction of Nitrobenzene under Conditions of Cyclic Voltammetry, J. Electroanal. Chem. **296**, 589 (1990).
298. Kayali I., Friberg S.E., Zuman P.: Interaction of Steroids with a Model of Stratum Corneum Lipids, Progr. Colloid Polymer Sci. **82**, 173 (1990).
299. Zuman P.: Redox Systems Generated by Electrochemical Oxidations and Reductions in “Selective Activation of Drugs by Redox Process” (G.E. Adams, A. Breccia, E.M. Fielden and P. Wardman, Eds), NATO ASI Series, Series A: Life Sciences, Vol. 198, p. 39, Plenum Press, New York 1990.
300. Zuman P.: A Review of Reactions of Some Sterols in Strongly Acidic Media, Microchem. J. **43**, 46 (1991).
301. Ellaithy M., Veivia D., Zuman P.: Anodic Waves of 9,10-Phenanthrenequinone in Alkaline Media, Microchem. J. **43**, 46 (1991).
302. Zuman P., Fijalek Z.: Addition of Hydroxide Ions to Nitrosobenzene: Equilibria and Some Reactions of the Adduct, J. Org. Chem. **56**, 5486 (1991).
303. Zuman P.: Reduction of Aromatic Nitro Compounds: The Fate of Arylhydroxylamines in “Electroorganic Synthesis”, Festschrift for Manuel M. Baizer, (R.D. Little and N.L. Weinberg, Eds), p. 137, M. Dekker, New York 1991.
304. Orienti I., Fini A., Zecchi V., Zuman P.: Diffusion of Naproxen in Presence of β-Cyclodextrin Across a Silicone Rubber Membrane, Pharm. Acta Helv. **66**, 204 (1991).
305. Rupp E., Zhong Q., Zuman P.: Polarographic Determination of Some Pesticides Containing Nitro Group: Application to a Study of Adsorption on Lignin, Electroanalysis **4**, 11 (1992).
306. Ellaithy M.M., Zuman P.: Electroreduction of Nifedipine, J. Pharm. Sci. **81**, 191 (1992).
307. Fini A., Fazio G., Tonelli D., Roda A., Zuman P.: Chemical Properties of Bile Acids V. Interaction with Concentrated Sulfuric Acid, Il Farmaco **47**, 741 (1992).
308. Kozlowski J., Zuman P.: Acid-Base, Hydration-Dehydration and Keto-Enol Equilibria in Aqueous Solutions of α-Ketoacids: Study by Spectroscopy, Polarography and Linear Sweep Voltammetry, Bioelectrochemistry and Bioenergetics **28**, 43 (1992); also J. Electroanal. Chem. **343**, 43 (1992).
309. Zuman P., Fijalek Z., Dumanović D., Sužnjević D.: Polarographic and Electrochemical Studies of Some Aromatic and Heterocyclic Nitro Compounds, Part I: General Mechanistic Aspects, Electroanalysis **4**, 783 (1992).
310. Dumanović D., Jovanović J., Sužnjević D., Erceg M., Zuman P.: Polaro-

graphic and Electrochemical Studies of Some Aromatic and Heterocyclic Nitro Compounds, Part II: Polarographic and Voltammetric Reduction of Some Nitramines, Pyrazolium and Imidazolium Nitro Derivatives, Electroanalysis **4**, 795 (1992).

311. Rupp E.B., Zuman P., Šestáková I., Horák V.: Polarographic Determination of Some Pesticides. Application to a Study of their Adsorption on Lignin, J. Agric. Food Chem. **40**, 2016 (1992).
312. Feroci G., Fini A., Zuman P.: Polarographic Study of the Interaction of Cholate aggregates with Cu^{2+}, Pb^{2+} and Cd^{2+} ions, Bioelectrochem. and Bioenergetics (J. Electroanal. Chem.) **29**, 91 (1992).
313. Dumanović D., Jovanović J., Sužnjević D., Erceg M., Zuman P.: Polarographic and Electrochemical Studies of Some Aromatic and Heterocyclic Nitro Compounds, Part III: Electroreduction of Mono- and Dinitropyrazoles and -Imidazoles, Electroanalysis **4**, 871 (1992).
314. Dumanović D., Jovanović J., Sužnjević D., Erceg M., Zuman P.: Polarographic and Electrochemical Studies of Some Aromatic and Heterocyclic Nitro Compounds. Part IV. Polarographic Reduction of 2-Alkylnitroimidazoles and Aminonitroimidazoles, Electroanalysis **4**, 889 (1992).
315. Zuman P.: J. Heyrovský and the Developments Leading to Square-Wave and Pulse Polarography, Analyst **117**, 1803 (1993).
316. Dumanović D., Jovanović J., Marjanović B., Zuman P.: Polarographic and Electrochemical Studies of Some Aromatic and Heterocyclic Nitro Compounds. Part V. Polarographic Reduction of Cyano- and Carboxamidonitropyrazoles, Electroanalysis **5**, 47 (1993).
317. Fijalek Z., Zuman P.: Polarographic and Electrochemical Studies of Some Aromatic and Heterocyclic Nitro Compounds. Part VI. Polarographic, Voltammetric and Controlled Potential Reduction of Ortho-Nitrobenzaldehyde and Anthranil, Electroanalysis **5**, 53 (1993).
318. Fijalek Z., Pugia M., Zuman P.: Polarographic and Electrochemical Studies of Some Aromatic and Heterocyclic Nitro Compounds. Part VIII. Polarographic, Voltammetric and Controlled Potential Electrolytic Reduction of Meta- and Para-Nitrobenzaldehyde, Electroanalysis **5**, 65 (1993).
319. Zuman P.: Electroreduction of Aromatic Nitrocompounds: Case for Comparison of Information Obtained by Polarography and Voltammetry, Collect. Czech. Chem. Commun. **58**, 41 (1993).
320. Fini A., Zuman P.: Spectrophotometric Determination of Bile Acids; an Evaluation, Collect. Czech. Chem. Commun. **58**, 53 (1993).
321. Zuman P., Fini A., Fazio G., Feroci G.: Interaction of Bivalent Metal Ions with Bile Salts in Redox Mechanisms and Interfacial Properties of Molecules of Biological Importance (F.A. Schultz and I. Taniguchi, Eds), Electrochem. Soc., Pennington, p. 175, New Jersey 1993.
322. Menzmer M., Zuman P.: Characterization of a Model for Consecutive First-

Order Reactions: Redox Chemistry of Bile Acids, Microchem. J. **48**, 158 (1993).

323. Rupp E., Zuman P.: The Use of Differential Pulse and D.C. Polarography in the Analysis of Solutions Containing Surfactants, Anal. Letters **27**, 939 (1994).
324. Privman M., Zuman P.: Kinetics of Hydrolysis of 1,3,5-Triazine in Mildly Acidic Media, Heterocycles **37**, 1637 (1994).
325. Dumanović D., Kosanović Dj., Zuman P.: Optimization of Synthesis of Nitroimidazoles and Nitropyrazoles Based on Polarographic Investigations, Heterocycles **37**, 2009 (1994); corrected version **41**, 1503 (1995).
326. Feroci G., Fini A., Fazio G., Zuman P.: The Role of Reaction Conditions in the Interaction of Cadmium(II) Ions with Cholate Anions, J. Colloid Interface Sci. **166**, 180 (1994).
327. Zuman P., Avramov-Ivić M., Adžić R.: A Study of the Oxidation of Benzaldehyde on Single Crystal Gold Electrodes and Comparison with Formaldehyde, J. Serb. Chem. Soc. **59**, 563 (1994).
328. Zuman P., Shah B.: Addition, Reduction, and Oxidation Reactions of Nitrosobenzene, Chem. Rev. **94**, 1621 (1994).
329. Zuman P., Karakus C.: Effect of Electronegative Substituents on Half-Wave and Peak Potentials of Nitrobenzenes in Aqueous and Mixed Solvents, Denki Kagaku **62**, 1306 (1994).
330. Privman M., Rupp E.B., Zuman P.: Hexazinone: Polarographic Reduction and Adsorption on Lignin, J. Agric. Food Chem. **42**, 2946 (1994).
331. Feroci G., Fazio G., Fini A., Zuman P.: Interaction between Cu^{2+} Ions and Cholic Acid Derivatives Followed by Polarography, J. Pharm. Sci. **84**, 119 (1995).
332. Zuman P., Rupp E.: Polarographic and Electrochemical Studies of Some Aromatic Nitro Compounds: Part VIIII. Effect of Solvents and Surfactants on Current-Voltage Curves Obtained with DC and Differential Pulse Polarography, Electroanalysis **7**, 132 (1995).
333. Zuman P., Rupp E.: Polarography in the Investigation of Alkaline Cleavage of Lignin, Soil Organic Matter and Humic Acid, Chem. Anal. (Warsaw) **40**, 549 (1995).
334. Feroci G., Fini A., Fazio G., Zuman P.: Interaction between Dihydroxy Bile Salts and Divalent Heavy Metal Ions Studied by Polarography, Anal. Chem. **67**, 4077 (1995).
335. Karakus C., Zuman P.: Polarographic and Electrochemical Studies of Some Aromatic and Heterocyclic Nitro Compounds. Part 9. Substituent Effects on Protonation of the Radical $ArNO_2H\cdot$ and its Reaction with Hydroxylamino and Nitroso Com61pounds in Buffered Mixtures of Water and DMF, J. Electroanal. Chem. **396**, 499 (1995).
336. Karakus C., Zuman P.: Electrosynthesis of Nitrosobenzenes Bearing Electron

Withdrawing Substituents, J. Electrochem. Soc. **142**, 4018 (1995).

337. Riedl F., Ludvík J., Volke J., Zuman P., Liška F.: Chemical and Electrochemical Transformation of 1,2,4-Triazine Herbicides in "Electrochemistry for Environmental Protection" (K. Štulík and R. Kalvoda, Eds), UNESCO Lab. of Environmental Electrochem., p. 153, Prague 1995.
338. Feroci G., Fini A., Fazio G., Zuman P.: Effect of Divalent Transition Metal Ions on the Aggregation of Trihydroxy Bile Salts, J. Colloid Interface Sci. **178**, 339 (1996).
339. Privman M., Zuman P.: Effect of Some Urea Derivatives on Measurement of pH with Glass Electrodes, Anal. Letters **29**, 687 (1996).
340. Zuman P., Rupp E., Privman M.: Role of Lignin in Adsorption of Some Toxic Materials and in Remediation in "EnviroAnalysis 1995" (R. Clement and R. Burk, Eds), p. 45, Ottawa 1996.
341. Fini A., Feroci G., Fazio G., Roda A., Zuman P.: Solution Behavior of Bile Salts in the Presence of Divalent Heavy Metal Cations, Current Topics in Soln. Chem. **1**, 69 (1994).
342. Zuman P.: Effect of Structure of the Reactive Species on Some Polarographic Processes, [in Czech], Chem. Listy **90**, 424 (1996).
343. Riedl F., Ludvík J., Liška F., Zuman P.: The Difference between the Reactivities of Azomethine Bonds in Metamitron in Electrochemical and Chemical Reductions, J. Heterocyclic Chem. **33**, 2063 (1996).
344. Zuman P., Rupp E.: Electrochemical Techniques in the Investigation of Interactions of Lignin with Pesticides and the Use of Lignin as Decontaminant, Electrochem. Soc. Proc. **95**, 267 (1995).
345. Feroci G., Fini A., Fazio G., Roda A., Zuman P.: Reactions of Small Aggregates of Taurine Conjugates of Dihydroxy Bile Salts with Divalent Transition Metal Ions, Microchem. J. **55**, 382 (1997).
346. Zuman P.: Polarography as a Tool for Investigations of Chemical Reactions Accompanying Electrode Processes, [in Czech] Chem. Listy **91**, 91 (1997).
347. Riedl F., Ludvík J., Volke J., Zuman P., Liška F.: Chemical and Electrochemical Transformations of 1,2,4-Triazine Herbicides in "Electrochemistry for Environmental Protection" (K. Štulík and R. Kalvoda, Eds), Unesco Venice Office (ROSTE), p. 191, Venice, 1996.
348. Shibata M., Zuman P.: Electroreduction of the Hydrazide of Maleic Acid in Aqueous Solutions, J. Electroanal. Chem. **420**, 79 (1997).
349. Fini A., Feroci G., Fazio G., Zuman P., Roda A.: Bile Sale Aggregates as Pre-Organized Substrates for Binding H^+ and Me^{2+} Ions in "Recettori Pre-Organizzati Per Metalli E Substrati" (A. Fini, Ed.), Acad. Sci. Istituto, p. 71, Bologna 1996.
350. Fini A., Feroci G., Fazio G., Zuman P.: Interactions of Dihydroxy Bile Salts with Some Divalent Metal Ions, Química Analitica **15** [Suppl. 1], 558 (1996).
351. Fini A., Feroci G., Breccia-Fratadocchi A., Fazio G., Zuman P.: Complexes

of Bile Salts: Study of the System Cd(II) – Cholate by means of Polarography, [in Italian] Atti della Acad. delle Sci. dell' Istituto di Bologna, U. Sci. Anno 283°, Rend. Ser. XIV, Tomo XII, p. 77, Bologna 1996.

352. Fini A., Feroci G., Fazio G., Zuman P.: Interaction of Iron(II) with Bile Salts, J. Inorg. Biochemistry **68**, 251 (1997).
353. Zuman P.: Half a Century of Research Using Polarography, Microchem. J. **57**, 4 (1997).
354. Zuman P., Bover J., Johnson C.: Electroreduction of Organic Compounds with Two Reactive Centers. II. Isophthaladehyde in "Novel Trends in Electroorganic Synthesis" (S. Torii, Ed.), p. 233, Springer Verlag, Tokyo 1997.
355. Zuman P., Riedl F., Liška F., Ludvík J.: Electroreduction of Organic Compounds with Two Reactive Centers. I. 1,2,4-Triazines in "Novel Trends in Electroorganic Synthesis" (S. Torii, Ed.), p. 337, Springer Verlag, Tokyo 1997.
356. Al-Bawab A., Friberg S.E., Zuman P., Sjoblöm J.: Reaction between Tetraethyoxysilane and Chloral Hydrate in Ethanol. A ^{29}Si NMR Investigation, J. Disp. Sci. Techn. **19**, 571 (1998).
357. Privman M., Zuman P.: The Role of Protonation, Hydration, Elimination, and Ring Opening in the Electroreduction of Hexazinone, J. Electroanal. Chem. **455**, 235 (1998).
358. Ludvík J., Riedl F., Liška F., Zuman P.: Electrochemical Reduction of Metamitron, J. Electroanal. Chem. **457**, 177 (1998).
359. Ludvík J., Riedl F., Liška F., Zuman P.: Electrochemical Reduction of Metribuzin, Electroanalysis **10**, 869 (1998).
360. Suznjevic D., Blagojevic S., Vucelic D., Zuman P.: Polarographic Determination of Hydrogen Peroxide in Perborate-Containing Commercial Detergents under the Bleaching Process Condition, Electroanalysis **9**, 861 (1997).

B. Monographs and Textbooks

1. Heyrovský J., Zuman P.: Introduction to Practical Polarography, [in Slovak], Prace, Bratislava 1950; [in Czech] NCSAV, Prague 1953; 2nd ed., 1964; [in Hungarian] Akad, Kiado, Budapest 1955; [in Polish] Panstw. Wydaw, Nauk, Warsaw 1956; [in German] Verlag Technik, Berlin 1959; [in English] Academic Press, London 1968.
2. Březina M., Zuman P.: Polarography in Medicine, Biochemistry and Pharmacy, Interscience, New York 1958, augmented German edition, Akad, Verlagsges. 1956; original Czech edition, SZN., Prague 1952.
3. Zuman P.: Principles of Polarography, [in Czech], Prirodoved, Vyd., Prague 1952.
4. Zuman P.: Effect of Structure on the Polarographic Behavior of Organic Substances, [in Czech], NCSAV, Prague 1954.
5. Zuman P.: Organic Polarographic Analysis, Pergamon, London 1964; [in Czech] SNTL, Prague 1966; [in Japanese] Kyoritsu Shuppan, Kyoto 1967.
6. Zuman P.: Substituent Effects in Organic Polarography, Plenum Press, New York 1967; [in Slovak] Alfa, Bratislava 1971.
7. Zuman P., Kolthoff I.M. (Eds): Progress in Polarography, Vols. I and II, Interscience, J. Wiley, New York 1962.
8. Zuman P.: The Elucidation of Organic Electrode Processes, Academic Press, New York 1969.
9. Zuman P., Perrin C.L.: Organic Polarography, Interscience, J. Wiley, New York 1969.
10. Zuman P.: Topics in Organic Polarography, Plenum Press, New York 1970.
11. Zuman P., Meites L., Kolthoff I.M. (Eds): Progress in Polarography, Vol. III, J. Wiley, New York 1972.
12. Meites L., Zuman P., Scott W.J., Campbell B.H., Kardos A.M.: Electrochemical Data, Part I, Vol. A, J. Wiley, New York 1974.
13. Meites L., Zuman P. *et al.*: Handbook Series in Organic Electrochemistry, Vols I and II, CRC Press, Cleveland, Ohio 1977; Vol. III, CRC Press, West Palm Beach, Florida 1978; Vols IV–VI, CRC Press, Boca Raton, Florida 1980–1983.
14. Meites L., Zuman P. *et al.*: Handbook Series in Inorganic Electrochemistry, Vol. I – VIII, CRC Press, Boca Raton, Florida 1980–1988.
15. Zuman P., Patel R.: Techniques in Organic Reaction Kinetics, J. Wiley, New York 1984, Krieger Publ. Co. 1992.