

Past, present, and future of applications of electroanalytical techniques in analytical and physical organic chemistry

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Abstract After a brief introduction describing the main milestones in the development of DC polarography (DCP) as well as linear sweep (LSV) and cyclic voltammetry (CV), attention is paid to first applications of DCP in the reduction of organic compounds. In aqueous solutions the electron transfer (ET) is often accompanied by a proton transfer. Limiting currents in DCP enable investigation of kinetics of chemical reactions preceding ET. Dependence of the limiting current on concentration of a reagent, like H^+ or OH^- ions, enables determination of rate constants (k) of very fast reactions, with k values between 10^4 and $10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$, comparable with those studied by relaxation methods. Application of CV is most advantageous for investigation of rates of chemical reactions following the ET. Comparison of analytical applications of DCP (reductions) with those of LSV (oxidations) is given. Apart from fast reactions taking place before the ET in the solution in

the vicinity of the electrode surface, DCP can also be used for investigation of slower reactions, taking place in the bulk of the solution. Data obtained by DCP for determination of equilibrium (K) and rate (k) constants of reactions of organic compounds. Hence, DCP can be used in physical organic chemistry of solutions, in some cases complementing data obtained by UV–vis spectrophotometry. Some examples of determinations of K and k are given. Uncertain future of practical analytical applications of DCP and LSV is discussed as is the brighter future of applications in physical organic chemistry. As the main factor limiting successful applications is considered the limited opportunity for education of future research advisors in academia and group supervisors in industry.

Keywords DC polarography · Linear sweep and cyclic voltammetry · Practical analysis · Physical organic chemistry, the use in · Reaction kinetics of fast reactions · Reaction kinetics of slower reactions · Rate constants · Equilibrium constants · Proton transfers · Additions of OH^- ions

Introduction

The first electroanalytical technique used in investigation of the oxidation–reduction behavior of organic compounds was potentiometry, in which the potential between an oxidized and reduced forms in equilibrium was determined at practically no passage of current. These investigations were limited to systems, where the equilibrium between the oxidized and reduced forms was established rapidly relative to the time interval of measurement. The observations were summarized in a monograph by L. Michaelis [1, 2]. The results led to one important conclusion, namely that the

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electron transfers are accompanied by proton transfers, involving the oxidized or the reduced forms or both.

Attempts during the second half of the nineteenth and first two decades of twentieth century to apply gradually increasing voltage and record the current to a solid, usually platinum, and a reference electrode did not yield reproducible results. In 1922, J. Heyrovský [3, 4] introduced to the electrolysis with gradually increasing voltage a dropping mercury electrode (DME) as the working electrode. This technique, developed at the Charles University in Prague, was named polarography. The growth of the use of polarography was facilitated by the invention of the polarograph, an instrument for automatic recording of current–voltage (i – E) curves. In the development of the instrument, using photographic recording of i – E curves, J. Heyrovský was supported by M. Shikata from Japan [5]. For some time, in the 1930s, Czechoslovakia and Japan became hubs of the research using polarography. Whereas the group in Prague (and sister groups in Warsaw and Bologna) concentrated predominantly on understanding processes at the DME and their applications in inorganic analysis, the Japanese group, particularly under the influence of I. Tachi, started to investigate electroreductions of organic compounds, among the first one the processes involved in the reduction of nitrobenzene [6]. The progress in these areas in Europe and Japan was interrupted by WWII.

The developments in the USA before the entry to WWII were affected by the American lecture tour of J. Heyrovský in 1933, which generated an interest in polarography. This interest was encouraged in 1939 by the manufacture of the first American polarographic instrument by the Sargent Company and by the publication in 1939 of a widely accepted monograph by the eminent American chemist, I.M. Kolthoff [7, 8], which appeared in second edition in 1952. That was followed by a monograph by L. Meites [9, 10].

In Europe, where at that time German was the predominant language used in chemical publications, the role of polarography has been widely accepted by the review of J. Heyrovský [11] in the Böttger series and by his monograph published by Springer [12]. All these publications contained relatively smaller sections dealing with the electrochemical behavior of organic compounds. Some contributions can be found in the monograph by G. Semerano published in Italian [13, 14].

Wider information about the types of electrode processes involving organic compounds were disseminated by the excellent review articles by S. Wawzonek published in the 1950s yearly in *Analytical Chemistry*. In them, the author not only critically evaluated published contributions dealing with organic polarography but in some instances also suggested interpretation of the presented experimental evidence.

In Europe, after 1945, an explosion of scientific activity took place, including studies of electroreductions and oxidations of organic compounds. Among contributing research groups can be named those in Germany (M.v. Stackelberg and his group in Bonn, K. Schwabe, H. Berg and their groups in Dresden and Jena), those of H. Lund and B. Nygard in Scandinavia, those of G. Charlot, A. Kirrman, and P. Souchay in France, of W. Kemula (who invented the hanging mercury drop electrode), and his group in Poland. Among the pioneers of organic polarography in the UK could be named the groups by Thirsk, R. Parsons and Peover and in Italy the groups in Bologna and later in Padova to name a few. In the USA, it was P. Elving who was the first to form a large school dealing with electrolysis of organic compounds. Among his collaborators, G. Dryhurst applied extensively organic polarography to investigation of the behavior of some biologically important compounds.

In the 1950s and 1960s, before the advent of an extensive use of separation techniques, polarography was among the five most frequently used analytical techniques in the world.

In 1948, R. Brdička [15, 16] pointed out the possibility to use polarographic data for correlations between the structure of organic compounds and their reactivity in aqueous solutions. The present author pointed out in a monograph [17] the wide scope of the use of such correlations using a Linear Free Energy Relationships. Electrochemical data, obtained in nonaqueous solutions involving solely a transfer of an electron in a reversible process, have been correlated with structure using quantum mechanical treatments.

As has been pointed out, reductions and oxidations of organic compounds are often accompanied by proton transfers in acid–base reactions. The role of acid–base reactions on polarographic current–voltage curves of organic compounds was first observed by R. Brdička and K. Wiesner [16] for a heterogeneous process involving colloidal platinum as catalyst. These two authors laid foundations for investigation of fast chemical reactions taking place before the uptake of the first electron in processes which are denoted as following a CE mechanism.

Three types of equilibria, which can be perturbed by the transfer of electrons, were in particular investigated: acid–base reactions, hydration–dehydration processes, and additions of hydroxide ions. The possibility to investigate the rate of the protonation, preceding the uptake of the first electron, is based on the principle that an acid form is reduced at more positive potentials than the conjugate base. Thus, when a reducible acid is investigated in a series of buffers of gradually increasing pH, a more positive wave is observed to decrease with increasing pH (Fig. 1). The plot of the limiting current as a function of pH has a shape of a

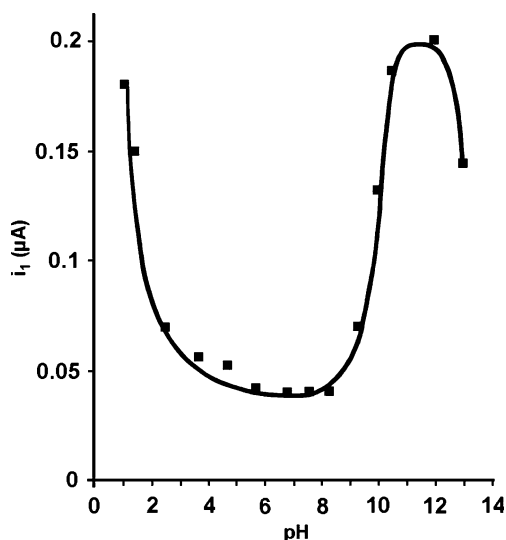


Fig. 3 Dependence of limiting currents of the more positive wave of reduction of the first CHO group is the unprotonated form of orthophthaldehyde in buffered solutions on pH. Increase of this wave at $\text{pH} < 4$ with decreasing pH is due to acid catalysis, the increase at $\text{pH} > 8$ (with increasing pH) to base catalysis. The decrease at $\text{pH} > 12$ is due to a formation of a geminaldiol anion, either by addition of OH^- to unhydrated CHO or by dissociation of $\text{CH}(\text{OH})_2$

formation of a carbinolamine, which is usually converted to an imine, which in some cases can undergo hydrolysis to yield a carbonyl compound—either the same as the starting one or a different one.

The last examples of the role of an addition in aqueous solutions are additions of hydroxide ions to a formyl group in some aromatic aldehydes. When these aldehydes are placed in a solution containing a sufficiently high concentrations of OH^- ions (usually above $\text{pH} 10$), a geminal diol anion is formed, which undergoes a two-electron oxidation to a carboxylate anion [22–24], from the anodic current in this pH range, where it increases with decreasing pH. From the $i=f(\text{pH})$ plot and the value of the equilibrium constant of the addition reaction, it is possible to calculate the rate constant of the addition reaction.

The second most frequently used electroanalytical technique is voltammetry, in which also the voltage is controlled and applied to a working and reference electrode (or a third electrode, when the resistance in the studied solution is higher), and the current is measured. Nevertheless, the rate of application of the voltage is much faster (from a few decades of V/s to thousands of V/s). The applied voltage either linearly increases with time (in linear sweep voltammetry, LSV) or first increases and then decreases with time (in cyclic voltammetry, CV).

During the exciting period after the end of WWII, CV was independently developed at the University of Birmingham in the UK by J. Randles [25] and at Charles University in Prague by A. Ševčík [26]. Even when the LSV or CV

experiments can be carried out during the life of a single drop, most frequently working electrodes used in these techniques are electrodes, the surface of which does not change with time. One such electrode is a hanging mercury drop electrode, but currently more frequently used are solid electrodes, such as various forms of carbon electrodes, as well as gold or silver electrodes.

Due to the high speed of the change of the applied voltage, numerous chemical reactions preceding the first electron uptake that can be studied using DC polarography do not play a role in LSV or CV. On the other hand, a product of electrolysis during the forward sweep may be followed on the reverse sweep. This enables the use of CV both in investigations of reversibility of the oxidation–reduction processes and for investigations of chemical reactions of products, formed during the forward sweep of voltage. Such types of reactions, taking place consecutively to an electron transfer, are denoted to follow an EC processes. In a limited number of cases, they can be studied using DC polarography but most often are investigated by CV.

In analytical applications of LSV, the peak current, which is usually a linear function of concentration, is measured. As analytical chemist is used to measure maximum and peak values, as in spectrophotometry, the acceptance of LSV is preferred, based on psychological reasons, to that of DC polarography (DCP), where limiting currents are measured. This obstacle is not present, where instead of $i-E$ curves, derivative curves $\Delta i/\Delta E$ are recorded or the shape of the voltage sweep is changed, in AC or in square wave polarography (SWP) where linearly increasing voltage is overlapped by square waves. Finally, in differential pulse polarography (DPP), the linear voltage is overlapped by a square wave and the current just before increase and toward the end of the increase is measured, and their difference is plotted as function of potential and recorded as in DPP.

The sensitivity of LSV is somewhat lower (typically used for 10^{-2} to 10^{-4} M solutions) than that of DCP (used for 10^{-3} to 10^{-5} M solutions). For trace analysis, the techniques like DPP or SWP has to be used, which enable analyses up to 10^{-8} M or even more diluted solutions.

The instrumentation used for LSV is simpler and cheaper than that needed when using DCP. In more demanding techniques, like DPP or SWP, synchronization of the current measurement with the drop-time is needed. Considerable advantage of the DCP is the high reproducibility of $i-E$ curves. Just one or few repeats of recorded $i-E$ curves are needed to obtain reliable results. The cleanliness of the electrode surface presents the essential problem of accuracy of results when LSV is used. The most frequently used carbon electrodes have to be mechanically cleaned—usually using fine sandpaper or another abrasive material.

For validation of results with carbon electrodes typically recording of five to 10 i - E curves are needed. When the drop-time (t_1) of a given capillary at given height of mercury column and the outflow rate of mercury in milligrams per second are stated, i - E curves recorded with DCP will be comparable anywhere in the world. For the use of LSV, validation of analytical results has to be established in every laboratory.

But the main difference between the applicability of DME and solid electrodes (such as carbon) is in the range of accessible potentials. Such range is limited towards negative potentials usually by potential of reduction of H^+ (up to about pH 10) and of alkali metal cations (or NH_4^+ cations) of the supporting electrolyte. Towards positive potentials the range is limited by the potential of oxidation of the mercury to mercury ions or of the metal forming the electrode or oxidation of oxygen or water.

Thus, DME and other mercury electrodes can be used up to -2.0 V or even -2.5 V towards negative potentials but only to about $+0.4$ V to positive ones. This is in contrast with carbon electrodes, which towards negative potentials can be used only up to about -1.1 V but up to $+1.2$ V toward positive potentials. Thus, the use of DME offers advantages towards negative potentials, whereas the use of the C-electrode in LSV offers mainly advantages when used at positive potentials. As numerous reductions take place at more negative potentials and most oxidations at positive ones, it can be understood that several thousands of reducible organic compounds has been investigated by DCP [27], but only several hundred ones of oxidizable organic species by LSV, most frequently using a carbon electrode.

In analytical applications, neither DCP nor LSV can compete with separation techniques in analyses of complex samples, as encountered in samples of biological (medical) materials and some natural products. But the speed, reproducibility, and sensitivity of DCP and related techniques can offer possibilities in analyses of drugs and in determination of some predominant contaminants in water analyses. The main hindrance of wider practical applications of electroanalytical methods is the scarcity of well-trained supervisors in industry and of knowledgeable advisors in academia in education of graduate students. Currently in the USA and in most European and Asiatic countries are missing research centers at the universities, which would educate graduate students specialized in electroanalytical chemistry. These students after graduation would teach the next generation of electroanalytical chemists. The policies of the NSF have had a negative impact, especially their preference for applied research, as, e.g., nanoparticle research and rather limited support of fundamental chemistry. And even if numerous common and widely used organic

electrode reactions are newly investigated in some detail, even an advanced chemist has to agree with Socrates' statement "I know that I know nothing." Present policy to limit research involving fundamental problems might lead to a situation that the USA and some Western European countries might be falling behind in chemical research. The basic electroanalytical chemistry needs support to educate a young generation of electrochemists who would be able to solve fundamental problems that will be found useful in practical applications.

One area, in which currently electroanalytical chemistry can offer some useful applications, is in physical organic chemistry. Thus, CV offers possibility to follow reactions of relatively unstable species that are generated by electroreduction or electrooxidation in EC processes. Alternatively, reestablishment of some equilibria, perturbed by electrolysis (reduction or oxidation), can offer information about the rate constants of fast reactions, involved in establishment of equilibria. This approach allows investigation of processes that follow a CE mechanism. The identification of such processes, the examples of which were discussed above, is of importance in separation studies, where the establishment of equilibria can affect the properties of the species during a passage through a column. But DC allows also a determination of equilibrium constants for equilibria that are extremely rapidly established. This is obtained by measuring the shifts of half-wave potentials and change of limiting currents of the electroactive species as a function of concentration of a component present in excess, for example of pH. On the other hand, it is possible to follow the changes of limiting currents of an electroactive species with variations of concentration of a reagent that is present in a relatively slowly established equilibrium. Hence, it is possible to record changes of limiting currents of C-acids with increasing pH. From dependence of the limiting current on pH, it is possible to obtain the pK_a values of C-acids [18–31]. Alternatively, it is possible to investigate reactions of carbonyl compounds with ammonia and primary amines. The imine formed in this reaction is in most instances reduced at more positive potentials than the carbonyl compound. Measuring the limiting current of the reduction of the imine at varying concentrations of the amine, it is possible to obtain the equilibrium constant of this reaction [32–34].

DCP does not enable to determine equilibrium constants for acid–base reactions, in which the equilibria that are perturbed by electrolysis are rapidly reestablished in the vicinity of the electrode. In such cases, the limiting current does not depend only on the diffusion of the electroactive species to the electrode surface but also on the rate of the recombination reaction. Determination of equilibrium constant is, nevertheless, possible using LSV. This application

is based on the possibility of varying in a wide range the rate of the applied voltage (the scan rate v). By increasing v , it is possible to eliminate from the current the component due to the rate of the recombination reaction. The resulting current is then strictly controlled by diffusion and proportional to the concentration of the electroactive species and can be used in calculation of the equilibrium constant. This approach has been used in determination of equilibria constants for hydration–dehydration equilibria involving formaldehyde [35] and 1,2-diketones [36].

As has been discussed above, DCP can be used for investigations of rates of fast reactions taking place within “reaction layer” in the vicinity of the electrode surface. But DCP, and in a lesser degree LSV, have also been used for investigation of much slower reactions, taking place in the bulk of the solution. In these applications, limiting current of a reactant is recorded as a function of time. If the electroactive species is the starting material, its limiting current is observed to decrease with time. The limiting currents of products increase with time. If an intermediate is electroactive, its limiting current first increases and then decreases with time.

The way of recording such time dependences depends on the reaction rate. For fastest reactions, with half-times between about 0.5 and about 3 min, the current at a constant potential corresponding to the plateau of the wave is continuously recorded. For reactions with half-time shorter than about 15 min, the current at a constant potential can be recorded for about 30 s at chosen time intervals. For still slower reactions, complete current–voltage curves in the potential region, where the wave is observed, are recorded after chosen time intervals. In this way, any changes in wave shape or formation of additional waves can be detected.

The data handling resembles that used for time variations of absorbances at chosen wavelengths in UV–visible spectra. In some instances, such applications of polarography and spectrophotometry are complementary.

As examples of applications of polarography in investigations of kinetics of organic reactions, taking place in the bulk of the studied solution are acid catalyzed hydrolyses of 1,3,5-triazines [37], dithiocarbamates [38], pyridoxal-5-phosphate [39, 40] dihydrometamitron [41], base catalyzed hydrolyses of isothiuronium salts [42, 43], cefepime [44], lignin [45], and carbimazole [46]. Among other studied reactions were investigated additions of hydroxide ions to nitrosobenzenes [47] and to α,β -unsaturated ketones [48], eliminations of Mannich bases [49], and their sulfone analog [50], as well as of hexazinone [51]. Among applications of DCP in elucidation of mechanisms were the proofs of formation of carbinolamine as an intermediate in additions of amines to aromatic aldehydes [52, 53].

So far, the situation in the past and present has been sketched. Now an attempt will be made to extrapolate the situation to the future.

For analyses of complex samples, such as blood, urine, tissues, as well as some natural products, HPLC, and other separation-based techniques will undoubtedly be the methods of choice. The only limitation of such procedures can be the fulfillment of the assumption that no chemical reactions will take place during the passage through the separatory column. DCP could, nevertheless, offer advantages in analyses of drugs, containing a single electroactive species and of heterogeneous samples, such as colloidal solutions or solutions containing suspended solid particles.

Let us hope that advantages DCP in following kinetics and equilibria in physical organic chemistry will be more widely recognized. In elucidation of even complex mechanisms of reactions in aqueous solutions, the combination with UV–visible spectra has proven to be particularly useful.

Currently, the main obstacle preventing wider use of electroanalytical techniques is the lack of well-trained advisors or supervisors. The proper application of electroanalytical methods assumes an understanding (at least in principle) of processes taking place at individual potentials on the used electrode. For this purpose, it is essential to learn and understand not only the electron transfers but also how the shapes of the current–voltage curves reflect the role of chemical reactions antecedent or sometimes also consecutive the electron transfers. It is important to understand how to determine the number of electrons transferred in each individual step and to distinguish, if any or how many proton transfers accompany the electron transfers. It is important to understand the solution chemistry of the species involved, in particular the nature of acid–base equilibria involved or that of complex formation. It is necessary to know how to determine the values of equilibrium and rate constants of the processes involved and understand approaches used in the elucidation of mechanisms of accompanying reactions. Understanding of structure–reactivity relationships and adsorption phenomena will be helpful.

The best place for acquiring such knowledge and educate future advisors and supervisors are in graduate schools that have groups specializing in electroanalytical chemistry. In past, such schools were numerous in the USA, for example at the University of/at Harvard, MIT, Minneapolis, Michigan, Iowa, Perdue, Austin, Kansas, Indiana, Cincinnati, Wisconsin, etc., in Canada in Sherebrooke, in UK at Bristol, Southampton, and Newcastle, in France in Paris, Dijon, and Rennes, in Germany in Bonn, Aachen, Dresden, Jena, and Greifswald, in Belgium in Brussels, in The Netherlands in Amsterdam and Utrecht, in Denmark in Aarhus, in Poland in Warsaw, in the Czech Republic in Prague and at Brno, in Italy in Bologna and Padova, in Croatia in Zagreb, in Serbia in Belgrade, in Turkey

in Ankara and Istanbul, etc. In each of these centers, there were one or two strong personalities, leaders, who coordinated the efforts of the group. It is to hope that such strong personalities with keep interest in organic electroanalytical chemistry and will develop and lead future research.

To finish, this author has to admit his joy in the academic success of his past students: Three of his Prague students became chairmen of Chemistry Departments at the universities in the USA, another one became the Director of the Heyrovský Institute of the Czech Academy of Science of Prague. His best student from his stay in the UK became a Professor at the University of Sydney (Australia) and his best student at Clarkson University became a Professor at the University of Connecticut. The latter one is currently ranked between the top ten electrochemists in the world. None of these mentioned above remained active in the area of present author, but by studying problems in electroanalytical chemistry, they learned how to contribute to the wider fields of chemistry. Out of his past collaborators, just one, Prof. J. Ludvík, is teaching electrochemistry at the Technical University in Prague and carrying research at the Heyrovský Institute in Prague and carries the flag of organic electroanalytical research further. His scientific grandchildren also already contribute to furthering applications of organic electroanalytical chemistry in various places around the world.

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