Stepwise electroreduction in voltammetry and chronopotentiometry

1 AUTHOR:

Rolando Guidelli
University of Florence

226 PUBLICATIONS **3,877** CITATIONS

motors (Superior Electric Co., Type SS 50-1008-P2) used to drive the glass syringe pumps. Pumping is interrupted during a tape reading cycle "Tape Advance Standby," or when the "Mixing Chamber Meniscus Control" senses the appropriate liquid level in the solvent mixing chamber.

Figure 4 shows a block diagram of the tape-controlled pumping system. The values of the desired solvent ratios, previously encoded on binary code tape, are processed by the "BCD Converters" and "Voltage Control Oscillators," shaped by translators (Trans), and their signals then activate the pulse-controlled stepping motors. These in turn drive the two-chamber syringe pumps in a linear motion, Four-way motor-driven valves (Hamilton Co., No. 4MMMM4) rotate at the end of each pump stroke, alternately connecting each syringe to filling and discharge lines. Limit switches (MS) control valve rotation and pump motor direction reversal. The solvents (DCM and PE) are kept water-saturated in sealed reservoirs and are displaced by the water pumped into them. This procedure eliminates solvent vapor pressure changes which develop when the solvents are pumped directly.

RESULTS AND DISCUSSION

Separations utilizing solvent gradients in column chromatography depend on the gradual polarity change as compounds are eluted. In effect, the small increments of increasing polarity prevent or minimize tailing between compounds, thus improving resolution. Precise control of the gradient is essential in resolution of compounds that differ only slightly in polarity. Less sophisticated apparatus for producing gradients is adequate for separating compounds with large polarity differences. Earlier studies in our laboratory showed that adrenocortical steroids had definite elution per cents that could be used in design of programmed separations (8) when using water-impregnated silicic acid and a PE–DCM gradient. Subsequent analysis of complex mixtures, following incubation of adrenal tissue with radioactive steroid precursors, presented a variety of radioactive products more complex than the standard mixture separated with the earlier equipment. The gradient system described here, with its capability of precisely controlling elution per cents to ±0.2%, facilitates separations not attainable previously.

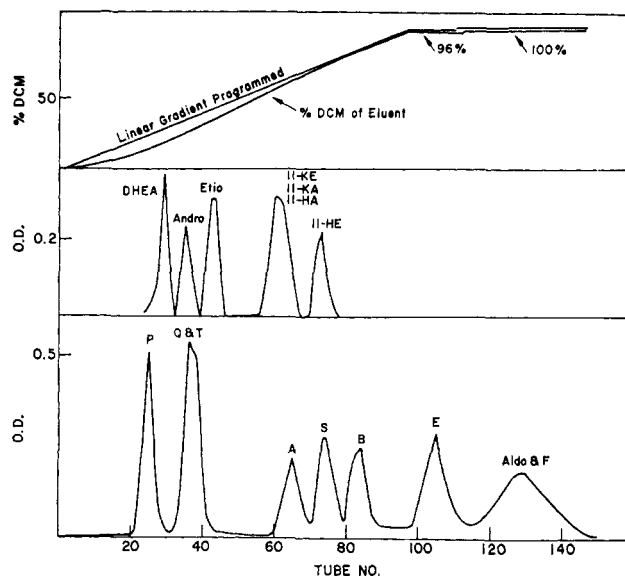(8) D. Francois, D. F. Johnson, and E. Heftmann, ANAL. CHEM., 35, 2019 (1963).

Figure 5. Programmed separation of adrenocortical and ketosteroids

See Reagents for nomenclature of standard compounds

Figure 5 shows the linear gradient used to separate adrenocortical and ketosteroids with this gradient system (7). Although each compound is not completely separated, the use of the linear gradient shown allows for the isolation of zones containing only a few compounds. These compounds can then be easily resolved and identified by thin-layer techniques. We previously reported on the use of different gradient programming and isolation of individual regions by using polarity reversal (1, 8).

The gradient elution system described has been used in our laboratory for separations of steroids, but it can easily be adapted to the analysis of other compound mixtures by proper choice of column support and solvent pairs.

ACKNOWLEDGMENT

The authors acknowledge the assistance of H. E. Cascio and H. W. Tipton for part of the technical development.

CORRESPONDENCE

# Some Considerations on Stepwise Electroreduction in Voltammetry and Chronopotentiometry

SIR: Quite often the compounds of elements characterized by several oxidation states yield voltammetric curves exhibiting several steps, due to the gradual electroreduction (or electrooxidation) of the element in question. Furthermore the case is frequently encountered in which during electrolysis some disproportionation equilibria are established near the electrode among the starting substance and the products of its electroreduction (or electrooxidation). In this connection, let us consider the general case of a sub-

stance A_1 which is electroreduced at the electrode surface in two successive steps, by the following overall electrode processes:

$$n_1 A_1 + n_1' e \rightarrow n_1'' A_2 \qquad (1a)$$

$$n_2 A_2 + n_2' e \rightarrow n_2'' A_3 \qquad (1b)$$
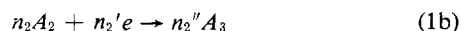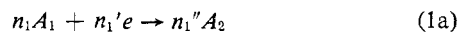
In Equations 1a and 1b A_2 is an intermediate product and A_3 the final product; n_1, n_1', n_1'', n_2, n_2', and n_2'' are stoichio-

metric coefficients. Let us assume that the three species A_1, A_2, and A_3 are involved in the disproportionation equilibrium:

$$\nu_1 A_1 + \nu_3 A_3 \rightleftharpoons \nu_2 A_2 \qquad (2)$$
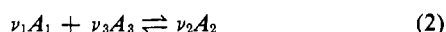
where ν_1, ν_2, and ν_3 are stoichiometric coefficients. According to the properties of Reaction 2, several cases can be encountered. Thus, if the equilibrium of Equation 2 is perfectly mobile and not too shifted to the right (e.g., the equilibrium $I^- + I_2 \rightleftharpoons I_3^-$ in aqueous solution), then the electroreduction of A_1 to A_3 takes place in a single step (1). Conversely, if Equilibrium 2 is perfectly mobile and markedly shifted to the right (e.g. the equilibrium $I^- + I_2 \rightleftharpoons I_3^-$ in acetic acid or in acetic anhydride) the overall electroreduction from A_1 to A_3 takes place in two quite distinct steps, both of them diffusion-controlled (1, 2). The case of a relatively slow Reaction 2 proceeding in a unidirectional way to the left [e.g. the disproportionation of H_2O_2 into H_2O and O_2 by the action of catalase in the electroreduction of O_2 to H_2O_2 on mercury (3)] can also be encountered. In this circumstance the limiting current of the first cathodic step $A_1 \rightarrow A_2$ may result in being partially controlled by the rate of the partial regeneration of the reactant A_1 from A_2 (catalytic current), in which case it is higher than the corresponding diffusion limiting current.

Here we shall limit ourselves to the consideration of the most frequently encountered case—namely, the case in which the current along the plateau separating the two partial waves $A_1 \rightarrow A_2$ and $A_2 \rightarrow A_3$ is diffusion-controlled. Under these conditions, independent of the mechanism by which Reaction 2 proceeds, we can state to a good approximation that along the rising portion of the second partial wave $A_2 \rightarrow A_3$, the volume concentration $\bar{C}_1$ of the reactant A_1 at the electrode surface is zero from the very beginning of electrolysis:

$$\bar{C}_1 = 0 \text{ for } t > 0 \qquad (3)$$

In Equation 3, t is the time elapsed from the start of electrolysis. It has been stated more than once (4, 5) that under the above conditions the limiting current of the partial wave $A_2 \rightarrow A_3$ is affected by Reaction 2. The aim of the present note is to show that, provided the diffusion coefficients of the species A_1, A_2, and A_3 may be considered to be equal, the limiting current of the partial wave $A_2 \rightarrow A_3$ is not at all influenced by the occurrence of Reaction 2 in the neighborhood of the electrode, regardless of whether this reaction is in equilibrium or not. Furthermore, if the electrode Reaction 1b is so fast that the Nernst equation can be applied to the concentrations of A_2 and A_3 at the electrode surface, then the whole rising portion of the partial wave $A_2 \rightarrow A_3$ is unaffected by the disproportionation Reaction 2.

Denote by z_1, z_2, and z_3 the oxidation numbers with which the electroactive element is present in the three compounds A_1, A_2, and A_3. Furthermore let l_1, l_2, and l_3 be the numbers expressing how many times an atom of the electroactive element is contained in a molecule of A_1, A_2, and A_3, respectively. With the preceding notations, the mass balance of Reaction 2 with respect to the atoms of the electroactive element is expressed by the equation:

$$\nu_1 l_1 + \nu_3 l_3 = \nu_2 l_2 \qquad (4)$$

The number of electrons that the atoms of the electroactive element contained in the compounds A_2 and A_3 have in excess with respect to the atoms contained in A_1 remains unaltered during the occurrence of the disproportionation Reaction 2. The above electron balance is expressed by the equation:

$$\nu_2 l_2 (z_1 - z_2) = \nu_3 l_3 (z_1 - z_3) \qquad (5)$$

By definition, the rate v of Reaction 2 is given by:

$$v = -\frac{1}{\nu_1} \frac{dC_1}{dt} = +\frac{1}{\nu_2} \frac{dC_2}{dt} = -\frac{1}{\nu_3} \frac{dC_3}{dt} \qquad (6)$$

In the most general case, v is a complicated function of C_1, C_2, and C_3 which, in their turn, are functions of the electrolysis time t and of the distance from the electrode surface.

The differential equations satisfied by the species A_1, A_2, and A_3 can be written in the following generalized form:

$$\delta C_1 = -\nu_1 v \text{ (a)}; \quad \delta C_2 = \nu_2 v \text{ (b)}; \quad \delta C_3 = -\nu_3 v \text{ (c)} \qquad (7)$$

where the expression for the operator δ depends on the mode of mass transport. Thus, for diffusion toward a planar stationary electrode we have:

$$\delta = \frac{\partial}{\partial t} - D \frac{\partial^2}{\partial x^2} \qquad (8)$$

where D is the diffusion coefficient common to the species A_1, A_2, and A_3 and x is the distance from the electrode surface. For diffusion toward a dropping electrode, δ is given by:

$$\delta = \frac{\partial}{\partial t} - D \frac{\partial^2}{\partial x^2} - \frac{2x}{3t} \frac{\partial}{\partial x} \qquad (9)$$

For diffusion toward a stationary spherical electrode we have:

$$\delta = \frac{\partial}{\partial t} - D \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \qquad (10)$$

where r is the distance from the center of the electrode. Finally, for mass transport toward a rotating disk electrode, δ is given by:

$$\delta = v_x \frac{d}{dx} - D \frac{d^2}{dx^2} \qquad (11)$$

where x is the distance from the disk electrode surface and v_x is the component of the fluid velocity normal to the electrode. In the absence of adsorption phenomena, the total flux of the atoms of the electroactive element which are contained in the three diffusing species A_1, A_2, and A_3 must be zero at the electrode surface. This statement is expressed by the following boundary condition:

$$l_1 \partial C_1 + l_2 \partial C_2 + l_3 \partial C_3 = 0 \qquad (12)$$

Here the operator ∂ is defined by:

$$\partial = (\partial/\partial x)_{x=0} \qquad (13)$$

for linear diffusion and for diffusion toward a dropping electrode. In the case of diffusion toward a stationary spherical electrode of radius r°, ∂ is defined by:

$$\partial = (\partial/\partial r)_{r=r^\circ} \qquad (14)$$

Finally, for mass transport toward a rotating disk electrode we have:

$$\partial = (d/dx)_{x=0} \qquad (15)$$

In the most general case the two other boundary conditions satisfied by the concentrations C_1, C_2, and C_3 along the rising portion of the partial wave $A_2 \rightarrow A_3$ are represented

(1) R. Guidelli and G. Piccardi, *Electrochim. Acta*, **12**, 1085 (1967).
(2) R. Guidelli and G. Piccardi, *Anal. Lett.* **1**, 779 (1968).
(3) J. Koutecký, R. Brdička, and V. Hanuš, *Collect. Czech. Chem. Commun.*, **18**, 611 (1953).
(4) F. C. Anson and J. J. Lingane, *J. Amer. Chem. Soc.*, **79**, 1015 (1957).
(5) P. Beran and S. Bruckenstein, ANAL. CHEM., **40**, 1044 (1968).

by Equation 3 and by an equation relating the flux of any of the two species A_2 and A_3 to the volume concentrations of these species at the electrode surface. This latter boundary condition can be written in the general form:

$$f(C_2, C_3, \partial C_2, \partial C_3) = 0 \text{ for } t > 0, x = 0 \text{ (or } r = r°) \quad (16)$$

The function f contains the kinetic parameters for the charge-transfer process Equation 1b and the applied potential E. If the electrode process (1b) has a high standard rate constant, then the boundary condition Equation 16 is replaced by the Nernst equation as applied to the concentrations of A_2 and A_3 at the electrode surface:

$$\frac{C_2{}^{n_2}}{C_3{}^{n_2{}''}} = \exp\left[\frac{n_2{}'F}{RT}(E - E°)\right] \equiv \theta \text{ for } t > 0,$$
$$x = 0 \text{ (or } r = r°) \quad (17)$$

In Equation 17 $E°$ is the standard potential of the A_2/A_3 couple.

In general the cathodic current density is given by the sum of the fluxes of the two electroreducible compounds A_1 and A_2, each flux being multiplied by the number of Faradays involved in the reduction of one mole of the corresponding compound. Hence the cathodic current is expressed by the equation:

$$i = FAD[l_1(z_1 - z_3)\partial C_1 + l_2(z_2 - z_3)\partial C_2] \quad (18)$$

where A is the electrode area. In view of Equation 7, the two linear combinations

$$\varphi = [C_2 + (\nu_2/\nu_1)C_1] \text{ (a)}; \quad \psi = [C_3 - (\nu_3/\nu_1)C_1] \text{ (b)} \quad (19)$$

satisfy the differential equations:

$$\delta\varphi = 0 \text{ (a)}; \quad \delta\psi = 0 \text{ (b)} \quad (20)$$

uncomplicated by kinetic terms. Furthermore from Equations 4, 5, 12, and 18, it immediately follows that the current i is proportional to the fluxes of the above combinations at the electrode surface:

$$i = FADl_2(z_2 - z_3)\partial\varphi = -FADl_3(z_2 - z_3)\partial\psi \quad (21)$$

In light of Equation 3 and of the definitions of φ and ψ, the boundary condition 17 can be written in the form:

$$\varphi^{n_2}/\psi^{n_2{}''} = \theta \text{ for } t > 0, x = 0 \text{ (or } r = r°) \quad (22)$$

Hence, provided the electrode process (1b) is fast, the solution of the boundary value problem Equations 3, 7, 12, and 17 is reduced to that of the simpler boundary value problem Equations 20–22. Since this latter problem does not contain the kinetic parameters relative to Reaction 2, it is evident that the partial wave $A_2 \rightarrow A_3$ is not influenced by this homogeneous reaction. The preceding considerations also hold in the case when the chronopotentiometric technique is employed. Thus the second potential-time step given by a solution of A_1 and due to the fast electrode process $A_2 \rightarrow A_3$ is not influenced by Reaction 2.

A somewhat different situation is encountered if the electrode process (1b) has a low standard rate constant, in which case the more general boundary condition Equation 16 applies. Under these circumstances, upon substituting φ and ψ from Equation 19 into Equation 16 and taking Equation 3 into account, we obtain an equation of the type:

$$f\left(\varphi, \psi, \partial\varphi - \frac{\nu_2}{\nu_1}\partial C_1, \partial\psi + \frac{\nu_3}{\nu_1}\partial C_1\right) = 0$$
$$\text{for } t > 0, x = 0 \text{ (or } r = r°) \quad (23)$$

Besides φ, ψ, $\partial\varphi$, and $\partial\psi$, the boundary condition Equation 23 contains ∂C_1, which in its turn is affected by Reaction 2. In fact the molecules of A_1 moving toward the electrode tend to react with the molecules of A_3 moving away from the electrode, with A_2 formation. In the present situation, the determination of the theoretical current–potential characteristic requires the solution of the three differential Equations 7a, 20a, and 20b and must account for the kinetics of the disproportionation Reaction 2.

When the voltammetric technique is employed, the concentrations of A_1 and A_2 at the electrode surface are zero along the plateau corresponding to the limiting current i_d of the total reduction wave of A_1 to A_3, regardless of whether the electrode process Equation 1b has a low or a high standard rate constant. Under these circumstances the boundary condition satisfied by φ is clearly given by:

$$\varphi = 0 \text{ for } t > 0, x = 0 \text{ (or } r = r°) \quad (24)$$

We then see from Equations 20a and 24 that the linear combination φ obeys a mass transport equation uncomplicated by kinetic terms and has a zero value at the electrode surface. The solution of the above boundary value problem is available in the literature for several modes of mass transport (6–8). Noting from Equation 21 that the current i is proportional to the gradient of φ at the electrode surface, we then have for the limiting current i_d:

$$i_d = FADl_2(z_2 - z_3)\varphi^*/\mu \quad (25)$$

where φ^* is the bulk value of φ and μ is the "Nernst layer" thickness. The expression for μ has differing forms depending on the particular mode of mass transport. Thus:

$$\mu = \sqrt{\pi Dt} \text{ for linear diffusion}$$

$$\mu = r°\sqrt{\pi Dt}/[r° + \sqrt{\pi Dt}] \text{ for spherical diffusion} \quad (26)$$

$$\mu = \sqrt{(3/7)\pi Dt} \text{ for diffusion toward a dropping}$$
electrode.

Furthermore, in the case of mass transport toward a rotating disk electrode, we have:

$$\mu = 1.80D^{1/3}\nu^{1/6}\omega^{-1/2}[0.8934 + 0.316(D/\nu)^{0.36}] \quad (27)$$

where ν is the kinematic viscosity of the solution and ω the angular velocity of the electrode. Upon denoting by C_1^* and C_2^* the bulk concentrations of A_1 and A_2 and taking Equations 4 and 5 into account, Equation 25 can be written in the form:

$$i_d = FADl_2(z_2 - z_3)\frac{(C_2^* + \nu_2C_1^*/\nu_1)}{\mu} =$$

$$FAD\frac{l_2(z_2 - z_3)C_2^* + l_1(z_1 - z_3)C_1^*}{\mu} \quad (28)$$

From Equation 28, it follows that, provided C_2^* is zero, i_d equals $FADl_1(z_1 - z_3)C_1^*/\mu$. Hence, taking into account that the diffusion limiting current $i_{d,1}$ for the first cathodic step $A_1 \rightarrow A_2$ is given by $i_{d,1} = FADl_1(z_1 - z_2)C_1^*/\mu$, the ratio between $i_{d,1}$ and the limiting current $i_{d,2} = i_d - i_{d,1}$ for the second cathodic step $A_2 \rightarrow A_3$ is simply given by

(6) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience, New York, N.Y., 1954, pp 49–63.
(7) J. Heyrovský and J. Kůta, "Principles of Polarography," Academic Press, New York, N.Y., 1966, pp 77–83.
(8) A. C. Riddiford, *Advan. Electrochem. Electrochem. Eng.*, **4**, 47 (1966).

$(z_1 - z_2)/(z_2 - z_3)$, regardless of whether Reaction 2 takes place or not. This conclusion contrasts with the interpretation of the experimental value for the ratio of the height of the oxidation wave from I^- to I_2 to the height of the successive oxidation wave from I_2 to IO_3^- in $1M$ $HClO_4$, as given by Beran and Bruckenstein (5).

We have seen that, if the standard rate constant for the electrode process Equation 1b is sufficiently high, then the boundary value problem relative to the partial cathodic wave $A_2 \rightarrow A_3$ involves exclusively the linear combinations φ and ψ and therefore is formally identical both when the solution contains either A_1 or A_2. Hence, under the present conditions, the second cathodic wave $A_2 \rightarrow A_3$ obtained from a solution of A_1 of concentration C_1^* is identical both in shape and in height to the unique cathodic wave given by a solution of A_2 of concentration $C_2^* = l_1C_1^*/l_2$. If the substance A_2 is not stable in solution or if its preparation is difficult, we can therefore advantageously study the properties of the $A_2 \rightarrow A_3$ step starting from a solution of A_1 without worrying about kinetic complications due to Reaction 2. The preceding considerations hold even if Equilibrium 2 is

perfectly mobile and may be easily extended to the case in which A_1 is electroreduced in more than two steps. An eventual deviation from the preceding theoretical expectations may be attributed to the existence of a notable difference among the diffusion coefficients of the various species. Thus, for example, the two successive reversible steps $I^- \rightarrow I_2$ and $I_2 \rightarrow ICl$ of the overall oxidation wave of I^- to ICl in hydrochloric acid medium on smooth platinum, exhibit different heights (9, 10) on account of the noticeable difference among the diffusion coefficients of I^-, I_2, I_2Cl^-, ICl, and ICl_2^-.

Institute of Analytical Chemistry   Rolando Guidelli
University of Florence
Florence, Italy

(9) A. L. Beilby and A. L. Crittenden, *J. Phys. Chem.*, **64**, 177 (1960).
(10) G. Piccardi and R. Guidelli, *ibid.*, **72**, 2782 (1968).

A Digital Potentiostat

Sir: Reported, for the first time, is an instrument for potentiostatic control of an electrochemical cell employing a new technique—digital current feedback. Digital current pulses, which can be scaled to read-out directly on a scaler the weight of sample oxidized or reduced, pass through the auxiliary electrode of the cell and are used to maintain a control-potential. The potential-control rise-time of this device is limited primarily by the RC characteristics of the cell and, to a minor extent, by the size of the digital current driver and the dead time between pulses. This development entirely obviates the need for elaborate phase-correcting networks presently required to prevent potentiostatic overshoot or oscillation. In addition, current–time information appears at the output of the device in the form of a pulse train and is thus directly computer compatible. The use of a current-to-voltage converter and a voltage-to-frequency converter required for computer compatibility with conventional analog systems is eliminated. Since the instrument operates simultaneously as a potentiostat, a current-to-frequency converter, and subsequently as a digital integrator, a new term—digipotentiograter, abbreviated DPI—has been coined to identify it. The title of this article may, however, find more general acceptance. The further advantages of this new design are improved sensitivity and stability, design simplicity, and a large reduction in costs for components and assembly. Extensive use of integrated circuits is made. Also the instrument size and weight are small and the power requirements are quite low.

The arrangement shown in Figure 1 is used to digitally maintain a control-potential and to digitally measure the charge transfer which occurs in an electrochemical reaction. Two charge sources are connected to the auxiliary electrode. One source injects charge digitally, while the other source, which is a constant current driver, extracts charge on a continuous basis. Both drivers are designed to deliver up to 1 mA of average current and to perform independently of the potential of the auxiliary electrode.

The cell reference electrode is connected to the positive terminal of a differential comparitor through a unity gain impedance coupling amplifier and the desired control-potential is applied to the negative terminal. Any positive output from the differential comparitor-balance detector initiates operation of the digital charge pump for fixed time periods and at rates determined by the charge demands of the cell. A local 500-kHz crystal clock furnishes digital injector drive intervals up to the clock frequency and therefore provides very good digital resolution. Since the charge demand sampling is made only during the times *between* possible injector drive intervals, the occurrence of a partial current drive interval is prevented.

The small value capacitor C_1 is attached from the reference electrode to the grounded working electrode to maintain potential-control when the cell is driven through its electrocapillary maximum potential.

Figure 2 illustrates the current and voltage response in time to a -500 mV to ground square-wave applied to the control input of the DPI when employing a capacitive-resistive simulated cell load. The digital current feedback pulses, which are initially applied at the clock frequency and thus appear as a blur on the time base selected, drive the control potential from -500 mV to ground. Once ground is reached, only occasional pulses are required to maintain the control-potential. These pulses have an average frequency of about 4 kHz and a displacement in the control-potential of approximately 10 mV. Note that, in this system, the descent time is limited only by the current capability of the digital charge source and by the dead time between pulses. The use of a 10-mA charge source would, for example, reduce the descent time by a factor of 10.

Figure 3 shows a repeat of the above experiment but now using a modified Matson *et al.* cell (*1*) and employing $0.01M$

(1) W. R. Matson, D. K. Roe, and D. E. Carritt, Anal. Chem., **37**, 1594 (1965).