DEVELOPMENT OF ITERATIVE METHODS FOR THE EXACT DETERMINATION OF ACID DISSOCIATION CONSTANTS AND SPECIFIC REACTION RATES IN VARIOUS IONIC OR ELECTROCHEMICAL SYSTEMS. A REVIEW

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This article is dedicated to Professor Sergio Roffia on the occasion of his retirement.

Theory and iterative methods for analysis of potentiometric titration data are presented in this paper. The methods concern titrations of (i) weak monoprotic acids, (ii) mixtures of weak acids with their conjugate bases (buffer solutions), (iii) mixtures of two monoprotic acids, (iv) solutions of polyprotic (di- and triprotic) acids with overlapping ionisation steps,

and (v) mixtures of two diprotic acids. Using equations derived without approximations and data exclusively resulting from the buffer region of a titration curve, it is possible to extract the accurate values of the concentration(s) and thermodynamic dissociation constant(s) of the titrated acid(s), even when the titration is stopped well before the end-point of the titration. The main principles of the iterative methods can also be applied to the evaluation of chronoamperometric curves for various electrochemical mechanisms (ECECE, ECE, irreversible, quasi-reversible, and CE). Thus, it is possible to extract the kinetic parameters k_1 and k_2 of an ECECE mechanism using exclusively chronoamperometric data. The analysis of the chronoamperometric curves for the other mechanisms (ECE, irreversible, quasi-reversible, and CE) permits the extraction of the corresponding kinetic parameters even when the values of the diffusion coefficient D and the effective area A of the electrode are not known. A review with 52 references.

Keywords: Acidity; Dissociation constants; Kinetics; Thermodynamics; Rate constants; Equilibria; Potentiometry; Chronoamperometry; Electrochemistry.

1. INTRODUCTION

Thermodynamic constants of acid-base equilibria (K_{diss}) and reaction rate constants (k) are very useful parameters for various chemical, electrochemical and technological applications. Some examples are given below.

It is known that catalytic methods can be used in analytical chemistry for determination of heavy metals. In those methods, weak acids, mainly polyprotic, are used. These acids, acting both as buffer and complexing agents, may enhance the catalytic action of the metal to be determined[1–6], while, at the same time, they suppress the catalytic action caused by other metal ions present in solution. In order to assess the masking effect caused by an acid, it is necessary to know the stability constants of various complexes between the acid and metal ions. However, the determination of stability of such complexes demands accurate values of the dissociation constants of the acid used as complexing agent.

The production of compact and smooth metal deposits is an important task in electroplating processes. Metal deposits of uniform thickness and physical properties may be obtained if weak acids are used as additives in the plating solution. Moreover, these additives may prevent dendritic growth and, in some cases, can modify certain physical properties of the electrodeposits[7–10]. The influence of those additives has proved to be dependent on the extent of their dissociation[11–13]. Therefore, the dissociation constant K_{diss} appears to be a very useful parameter in explaining inhibition effects in the growth mechanism.

Finally, there is a large number of electrochemical reactions where both charge-transfer and chemical reactions are involved in the reaction mecha-

nism[14]. Typical electrode reactions with coupled homogeneous chemical reactions are the so-called CE, EC, ECE, and catalytic mechanisms[14,15]. Such systems are very common in organic electrochemistry. More complex mechanisms have also been reported. One example is the ECECE mechanism where three rapid charge-transfer steps are separated by two slow chemical reactions[16–18]. Depending on the sequence of steps involved and the values of the rate constants, the chemical steps may exert a dominant effect on the polarisation behaviour of the system.

The few examples reported above clearly show that thermodynamic constants of ionic equilibria or reaction rate constants are very useful parameters in quantitative analyses of various chemical and/or electrochemical systems. In this respect, techniques for accurate determination of such parameters have been developed during the last two decades in our laboratory. The basic principles of these methods are reviewed in the present article.

2. SIMULTANEOUS DETERMINATION OF EQUIVALENCE VOLUMES AND THERMODYNAMIC DISSOCIATION CONSTANTS OF WEAK ACIDS FROM POTENTIOMETRIC TITRATION DATA

The determination of the thermodynamic dissociation constants of weak acids can be realised by several methods. The most common procedure is the potentiometric titration. A variety of computational methods analysing potentiometric titration data were developed in the past few decades. Some of these methods are reported in excellent textbooks[19–21].

The majority of the methods reported in literature are valid when: (i) the titrations are carried out under conditions of constant ionic strength and (ii) the accurate value of the analytical concentration of the titrated acid is known. The first condition is satisfied by addition of sufficient amounts of a neutral salt. However, the obtained pK values under such conditions are not free of any possible “salt effect”. On the other hand, it has been argued in the literature that in media of high ionic strengths, even in the absence of a salt effect, the prediction of the activities of the various ionic species becomes inaccurate; the higher the ionic strength at which measurements are made, the more serious the difficulties in obtaining the dissociation constants become[22]. Concerning the analytical concentration of the titrated acid, this quantity is usually determined from the equivalence point of the titration curve. However, in some potentiometric titrations with a glass electrode in mixed water–organic solvent systems, the titrations curves of various weak acids do not show a pronounced vertical portion

corresponding to the end-point of neutralisation. On the other hand, the existence of multiple peaks in the immediate vicinity of the equivalence point of differential titration curves introduces an uncertainty in the choice of the exact value of the equivalence volume[23]. This behaviour could be attributed to two facts. First, the process of obtaining derivatives from experimental data usually results in considerably decreased accuracy[24]. Second, in the vicinity of the equivalence point, the response of the glass-calomel electrode set is slower than that observed in the buffer region of the same titration curve. Hence, in such solvent systems, it is very difficult to locate the end-point of the titration and to determine (or check) the accurate value of analytical concentration of the acid particular because of the contribution of hydrolysis of the salt formed. In addition, for some very weak acids, the equivalence volume does not coincide with the inflection point of the titration curves; the difference is the greater, the weaker is the acid[19,25].

In an attempt to overcome these difficulties, new iterative techniques have been developed in our laboratory, permitting simultaneous determination of the thermodynamic constant and the analytical concentration of weak acids[23,26]. Thus, we have obtained theory and methods of analysis of potentiometric titration data for (i) weak monoprotic acids, (ii) mixtures of weak acids with their conjugate bases (buffer solutions), (iii) mixtures of two monoprotic acids, (iv) solutions of polyprotic (di- and triprotic) acids with overlapping ionisation steps, and (v) mixtures of two diprotic acids. These methods, using equations derived without approximations and data exclusively resulting from the buffer region of a titration curve, seem to be valid throughout the acid strength range. It is noted that all these methods can successfully be employed for titrations with absent sharp end-point, or for the determination of analytical concentrations and pK of a moderately weak acid in the presence of other very weak acids, the neutralisation of which is undesirable. The latter determination can easily be done by stopping the titration well before the end-point.

2.1. Potentiometric Titration of Weak Monoprotic Acids with Strong Bases

Consider a volume V_o of any weak monoprotic acid HA of initial concentration C_o, which is titrated with a strong base MOH of concentration C_B. Assuming that all singly charged ions have the same activity coefficient γ_1 and that the activity coefficients of uncharged species are unity, the thermodynamic acid constant of HA is given by Eq. (*1*).

$$K_a = \frac{a_H[A^-]\gamma_1}{[HA]} \qquad (1)$$

At any point in the buffer region of the titration curve, the mass and charge balance are expressed by Eqs (*2*) and (*3*)

$$C = [HA] + [A^-] \qquad (2)$$

$$[H^+] + [M^+] = [A^-] + [OH^-] , \qquad (3)$$

where the concentrations C and $[M^+]$ can be determined from the equations:

$$C = \frac{C_B V}{V_o + V} = b_N C_B V_e$$

$$[M^+] = \frac{C_B V_e}{V_o + V} = b_N C_B V , \qquad (4)$$

where V is the volume of the added titrant, V_e the equivalence volume and $b_N = 1/(V_o+V)$.

Combining these equations gives after rearrangement:

$$a_H\left(b_N C_B V\gamma_1 + a_H - \frac{K_w}{a_H}\right) = K_a\left[b_N C_B (V_e - V) - \frac{a_H}{\gamma_1} + \frac{K_w}{a_H \gamma_1}\right]. \qquad (5)$$

K_w is the autoprotolysis constant of the solvent used. For dilute solutions (I < 0.1 M) the activity coefficient γ_1 can be calculated from the Debye–Hückel equation:

$$\log \gamma_1 = -\frac{Az_i^2\sqrt{I}}{1 + Ba^o\sqrt{I}} , \qquad (6)$$

where A and B are constants, the values of which depend on the physical properties of the medium[27], I is the ionic strength of the solution, z_i the

charge number and a^o the distance of closest approach of the ions. In principle, a^o is a function of the solvent and electrolyte, but in the practice it is traditionally taken to be equal to 5 Å [20,28,29]. The ionic strength, at any point of the titration curve, is given by Eq. (*7*)[20,30]:

$$I = [M^+] + [H^+] = b_N C_B V + [H^+] . \quad (7)$$

To determine γ_1, it is obviously necessary to know the value of $[H^+] = a_H/\gamma_1$ and *vice versa*. The values of $[H^+]$ and γ_1 can be obtained from the measured value of a_H (pH = –log a_H) by successive approximations. Assuming first $\gamma_1 = 1$, so that $a_H = [H^+]$, it is possible to calculate I from Eq. (*7*), and hence γ_1 from Eq. (*6*). This new value of γ_1 can be used to refine the values of $[H^+]$, I and γ_1. All these operations are repeated until γ_1 converges (the criterion here being less than 0.00001 difference in I, between two subsequent cycles).

It is noted that Eq. (*5*), including the thermodynamic dissociation constant of the titrated acid, is also valid under conditions of varying ionic strength during the titration. Equation (*5*) has then the form

$$Y = K_a X . \quad (8)$$

This equation predicts a linear relationship between Y and X with a slope equal to K_a. Alternatively, the experimental confirmation of such a correlation, using V and pH data, supports the assumption that the titrated acid is a monoprotic one. Then, the thermodynamic constant K_a can be deduced, by linear regression, from the slope of the corresponding straight line.

However, there is no way in which, without prior knowledge of V_e, the Y *vs* X data may be plotted to give a linear graph. However, this is possible with the iterative method proposed in this investigation. This procedure is analogous to previously proposed techniques for the determination of rate constants of SN2 reactions between ions and dipolar molecules in solvents where the ionic reactant associates to form ion pairs[31–34].

2.1.1. Iterative Method for the Determination of V_e and K_a

We assume first that the value of V_e lies in an interval (a,b). Choosing arbitrarily from this interval a value for V_e, it is possible to trace, by means of

the experimental V and pH data, the curve $Y = f(X)$. This will approach a straight line to the extent where the chosen value of V_e also approaches the exact value of the equivalence volume. So, the best linearity that could be obtained using the available experimental data, corresponds evidently to the best approximation to the exact value of the equivalence volume. So, by seeking the V_e value within the interval (a,b), it is possible to trace N curves $Y = f(X)$, N being the number of estimations of V_e values taken arbitrarily for these calculations. For each of these curves, the calculation of the squared correlation coefficient R^2 permits to compare the linearity of various $Y = f(X)$ plots and trace the curve $R^2 = f(V_e)$. This curve is expected to present a pronounced maximum at a value of V_e equal to V_e^{max} that can be considered as the best approximation to the exact value of the equivalence volume. The slope of the corresponding to V_e^{max} straight line is the best approximation to the exact value of K_a. It is noted that this iterative procedure is a general method that can be applied, as shown below, even to more complicated titrations (*i.e.*, mixtures of two acids). However, in the titrations of weak monoprotic acids, V_e and K_a can be more easily determined by the following graphical method.

2.1.2. Graphical Method for the Determination of V_e and K_a

Equation (*5*) can be rewritten as

$$y = V_e - \frac{1}{K_a} x \,, \tag{9}$$

where

$$y = V + \frac{1}{\gamma_1 C_B b_N} \left\{ a_H - \frac{K_w}{a_H} \right\} \tag{10}$$

and

$$x = a_H \left\{ \gamma_1 V + \frac{a_H}{C_B b_N} - \frac{K_w}{a_H C_B b_N} \right\} . \tag{11}$$

In this treatment, it is possible to determine V_e and K_a by linear regression from the coefficients of Eq. (*9*). It is noted that an analogous graphical procedure has been proposed by Johanson[35]. However, that approach focused rather on the determination of V_e, than of K_a. Indeed, in the Johanson method, the proposed equation, including the apparent dissociation con-

stant of the titrated acid, is valid under conditions where the ionic strength remains constant during the titration. This condition is normally fulfilled by addition of a neutral salt in sufficient amount. The difficulties arising in the determination of the thermodynamic K_a in such media values were discussed previously.

2.2. Potentiometric Titration of a Solution Containing a Conjugate Acid-Base Pair

Consider a volume V_o of a solution containing a conjugate acid-base pair, where the initial analytical concentrations of the weak acid HA and its conjugate base are respectively equal to C_o and C_b^o. This mixture can be considered as being prepared by partial neutralisation of a solution of the acid HA, of concentration C_o' and volume $V_o - Z$, with Z ml of a solution of a strong base MOH of concentration C_B. At any point of the titration curve, mass and charge balance are expressed by the equations:

$$[A^-] + [OH^-] = [M^+] + [H^+] \tag{12}$$

$$T_L = [HA] + [A^-] , \tag{13}$$

where

$$[M^+] = \frac{C_B V}{V_o + V} + \frac{C_b^o V_o}{V_o + V} = b_N C_B (Z + V) \tag{14}$$

$$T_L = \frac{T_L^o V_o}{V_o + V} + \frac{(Z + V_e) C_B}{V_o + V} = b_N C_B (Z + V_e) . \tag{15}$$

Combining Eqs (*1*), (*12*)–(*15*), one obtains

$$y = V_e - \frac{1}{K_a} x' . \tag{16}$$

In this equation, y is again given by Eq. (*10*), while x' is determined from the following equation:

$$x' = a_H \left\{ \gamma_1 (V + Z) + \frac{a_H}{C_B b_N} - \frac{K_w}{a_H C_B b_N} \right\} . \tag{17}$$

At any point of the titration curve, the activity coefficient γ_1 can be calculated from Eq. (*6*), where the ionic strength is given by

$$I = [M^+] + [H^+] = b_N C_B (Z + V) + [H^+] . \qquad (18)$$

As previously, the values of $[H^+]$ and γ_1 may be obtained from the measured pH values by successive approximations.

Equation (*16*) predicts a linear relationship between y and x' with a slope equal to $1/K_a$. Alternatively, the experimental confirmation of such a correlation, using the V and pH data, supports the assumption that the titrated solution is a mixture of a monoprotic acid with its conjugate base. Then, V_e and K_a can be deduced, by linear regression, from the coefficients of Eq. (*16*). This procedure can be realised by the presently proposed iterative method.

It is assumed first that the value of Z lies in an interval (a,b). Choosing arbitrarily from this interval a value for Z, it is possible to trace, using the experimental V and pH data, the curve $y = f(x')$. This curve will approach a straight line to the extent where the chosen value of Z also approaches the exact value of this parameter. Hence, the best linearity that could be obtained, using the available experimental data, evidently corresponds to the best approximation to the exact value of Z. Therefore, by seeking the Z value within the interval (a,b), it is possible to trace N curves $y = f(x')$, N being the number of Z values taken for these calculations. For each of these curves, the calculation of R^2 (square of the correlation coefficient) and S_{yx} (standard error of the estimate) permits a comparison of the linearity of various $y = f(x')$ plots and trace the curves $R^2 = f(Z)$ or $S_{yx} = f(Z)$. These curves must present respectively a maximum and minimum at a value of Z equal to Z_m, which can be considered as the best approximation to the exact value of Z. The exact values of V_e and K_a can be deduced, respectively, from the y-intercept and the slope corresponding to Z_m straight line.

2.3. Potentiometric Titration of Mixtures of Two Weak Monoprotic Acids with Strong Bases

The titration of mixtures of acids is a problem that was treated by numerous workers in the past. Two acids in a mixture with each other can simply be titrated if their pK values differ sufficiently. In such instances, the acids are neutralised serially in accord with their pK values. As a rule of thumb, a difference between the pK greater than 2 pK units is usually satisfactory to distinguish, by traditional titration, the component acids. For a smaller dif-

ference between the pK values, the acids are apparently neutralised simultaneously and the evaluation of the titration becomes increasingly difficult, yielding less reliable results. During the last decades, a wide variety of solutions to the problem were suggested[36–42]. All these methods require exact knowledge of the dissociation constants of the acids and most of them also require the sum of the concentrations of the acids. This situation has encouraged us to develop a new method permitting the simultaneous determination of the thermodynamic dissociation constants and the concentrations of two monoprotic acids in a mixture with each other even when the difference between their pK values is small. In this method, which requires only data resulting from the acid region of the titration curve, the sum of the concentrations need not be known.

Consider a volume V_o of a mixture of n weak monoprotic acids HA_1, HA_2, ..., HA_n of initial concentrations C_1^o, C_2^o, ..., C_n^o which is titrated with a solution of a strong base MOH of concentration C_B. Assuming again that all singly charged ions have the same activity coefficient γ_1 and that the activity coefficients of uncharged species are unity, the dissociation constant of the acid HA_i is expressed by Eq. (*19*):

$$K_i = \frac{a_H[A_i^-]\gamma_1}{[HA_i]} . \qquad (19)$$

At any point of the acidic region of the titration curve, mass and charge balance are expressed by the following equations:

$$\left.\begin{aligned} C_{tot} &= \sum_{i=1}^{n}[HA_i] + \sum_{i=1}^{n}[A_i^-] \\ \sum_{i=1}^{n}[A_i^-] &= [M^+] + [H^+] - [OH^-] = F \end{aligned}\right\}, \qquad (20)$$

where

$$C_{tot} = \sum_{i=1}^{n} C_i = \frac{C_{tot}^o V_o}{V_o + V} = \frac{C_B V_e}{V_o + V} = b_N C_{tot}^o V_o = b_N C_B V_e \qquad (21a)$$

$$C_{tot}^o = \sum_{i=1}^{n} C_i^o = \frac{C_B V_e}{V_o} \qquad (21b)$$

$$C_i = [\mathrm{HA}_i] + [\mathrm{A}_i^-] = [\mathrm{HA}_i]\left(1 + \frac{K_i}{a_\mathrm{H}\gamma_1}\right) = b_\mathrm{N} C_i^\mathrm{o} V_\mathrm{o} \qquad (21c)$$

$$F = [\mathrm{M}^+] + [\mathrm{H}^+] - [\mathrm{OH}^-] = b_\mathrm{N} C_\mathrm{B} V + \frac{a_\mathrm{H}}{\gamma_1} - \frac{K_\mathrm{w}}{a_\mathrm{H}\gamma_1} \qquad (21d)$$

Combination of Eqs (*19*)–(*21*) gives

$$C_\mathrm{tot} - F = \sum_{i=1}^{n} \frac{C_i}{1 + \frac{K_i}{a_\mathrm{H}\gamma_1}} \,. \qquad (22)$$

For $n = 2$, Eq. (*22*) yields

$$Y = A_0 + A_1 X_1 + A_2 X_2 \,, \qquad (23)$$

where

$$\left.\begin{aligned} &A_0 = K_1 K_2 \qquad A_1 = K_1 \qquad A_2 = K_2 \\ &Y = (a_\mathrm{H}\gamma_1)^2 \frac{F}{L} \qquad X_1 = a_\mathrm{H}\gamma_1 \frac{b_\mathrm{N} C_1^\mathrm{o} V_\mathrm{o} - F}{L} \qquad X_2 = a_\mathrm{H}\gamma_1 \frac{b_\mathrm{N}(C_\mathrm{tot}^\mathrm{o} - C_1^\mathrm{o})V_\mathrm{o} - F}{L} \\ &L = C_\mathrm{tot} - F = b_\mathrm{N} C_\mathrm{B}(V_\mathrm{e} - V) - \frac{a_\mathrm{H}}{\gamma_1} + \frac{K_\mathrm{w}}{a_\mathrm{H}\gamma_1} \end{aligned}\right\} . \qquad (24)$$

The activity coefficient γ_1 introduced in the above relationships can be determined, as previously, from Eq. (*6*) by successive approximations. Concerning the ionic strength I, a simple calculus gives

$$I = b_\mathrm{N} C_\mathrm{B} V + \frac{a_\mathrm{H}}{\gamma_1} \,. \qquad (25)$$

Equation (*23*) predicts that the relationship $Y = f(X_1, X_2)$ is linear. Alternatively, the experimental confirmation of such a correlation, using V and pH data, supports the assumption that the titrated solution is a mixture of two monoprotic acids. Then, the thermodynamic acidity constants K_1 and

K_2 may be obtained by a multiple linear regression method from the partial regression coefficients.

But, despite the fact that Eq. (*23*) offers a theoretical basis to correlate the results, there is no way in which, without prior knowledge of V_e (or C^o_{tot}) and C^o_1, the X_1 and X_2 data may be determined. This is possible with the iterative method proposed in this investigation.

This method is based on the particular property of Eq. (*23*) that, at the true value of the equivalence volume V_e defined by Eq. (*21b*), this equation is linear, independent of the chosen value C^o_1. Indeed, in the particular case where one uses the correct value V_e and an erroneous value for C^o_1 equal to $\hat{C}^o_1 = C^o_1 + \delta C^o_1$, the variables X_1 and X_2 are transformed into $\hat{X}_1$ and $\hat{X}_2$ defined by the following equations:

$$\hat{X}_1 = a_H \gamma_1 \frac{b_N \hat{C}^o_1 V_o - F}{L} = X_1 + \frac{a_H \gamma_1 b_N V_o}{L} \delta \hat{C}^o_1 \qquad (26)$$

$$\hat{X}_2 = a_H \gamma_1 \frac{b_N (C^o_1 - \hat{C}^o_1) V_o - F}{L} = X_2 - \frac{a_H \gamma_1 b_N V_o}{L} \delta \hat{C}^o_1 \ . \qquad (27)$$

Combination of Eqs (*24*), (*26*), and (*27*) yields

$$\frac{a_H \gamma_1 b_N V_o}{L} = \frac{\hat{X}_1 - \hat{X}_2}{2(C^o_1 + \delta C^o_1) - C^o_{tot}} \qquad (28)$$

and combination of Eqs (*23*), (*26*)–(*28*) gives

$$Y = \hat{A}_0 + \hat{A}_1 \hat{X}_1 + \hat{A}_2 \hat{X}_2 \ , \qquad (29)$$

where

$$\left.\begin{aligned} \hat{A}_0 &= A_0 = \hat{K}_1 \hat{K}_2 \\ \hat{A}_1 &= K_1 + \frac{(K_2 - K_1)\delta C^o_1}{2(C^o_1 + \delta C^o_1) - C^o_{tot}} \\ \hat{A}_2 &= K_2 - \frac{(K_2 - K_1)\delta C^o_1}{2(C^o_1 + \delta C^o_1) - C^o_{tot}} \end{aligned}\right\} \qquad (30)$$

It follows from these equations that, using the true value of V_e and any value for C_1^o, the relationship $Y = f(\hat{X}_1, \hat{X}_2)$ remains linear. However, the corresponding coefficients $\hat{A}_1$ and $\hat{A}_2$ are quite different from those of Eq. (*23*); the differences are greater, the greater is the value of δC_1^o. In the case when $\delta C_1^o = 0$, so that the selected value for C_1^o is the correct one, both Eqs (*29*) and (*23*) are identical. This very important property may be used to determine the values of V_e and C_1^o as follows.

It is assumed first that V_e is unknown and that its true value lies in an interval (a,b). Let $\hat{C}_1^o$ be any trial value for C_1^o chosen arbitrarily from an interval (a',b') of the possible values for this concentration. Starting from this value, and taking from the interval (a,b) any value for V_e, it is possible to obtain, using the experimental V and pH data, the dependence $Y = f(\hat{X}_1, \hat{X}_2)$. The latter will approach a linear relationship to the extent where the chosen V_e also approaches the exact value of the equivalence volume. Thus, the best linearity which can be obtained, using the available experimental data, corresponds evidently to the best approximation to the exact value of the equivalence volume. Hence, by seeking within the interval (a,b) the V_e value, it is possible to obtain N relationships $Y = f(\hat{X}_1, \hat{X}_2)$, N being the number of V_e values taken for these calculations. For each of these relationships, the calculation of the squared multiple correlation coefficient R^2 allows to compare the linearity of the various $Y = f(\hat{X}_1, \hat{X}_2)$ variations and to trace the curve $R^2 = f(V_e)$. This is supposed to present a pronounced maximum at a value of V_e equal to V_e^{max}, which can be considered the best approximation to the exact value of the equivalence volume. At this value of V_e, the partial regression coefficients of the corresponding multiple regression equation will approach the coefficients of Eq. (*23*) to the extent where the chosen value $\hat{C}_1^o$ also approaches the exact value of C_1^o. In a second step, starting from the value V_e^{max}, and seeking within the interval (a',b') the $\hat{C}_1^o$ value, it is possible to obtain, as above, N' relationships $Y = f(\hat{X}_1, \hat{X}_2)$, N' being the number of $\hat{C}_1^o$ values taken for these calculations. For each of these relationships, it is possible to calculate the ratio

$$R_{cf} = \frac{\hat{A}_0}{\hat{A}_1 \hat{A}_2} . \qquad (31)$$

This ratio may be equal to unity at a certain value of $\hat{C}_1^o$ that can be considered as the best approximation to the exact value of C_1^o. Evidently, C_2^o can be calculated from Eq. (*21b*), while pK_1 and pK_2 can be estimated from the coefficients of the corresponding multiple linear regression equation.

2.4. Potentiometric Titration of Weak Polyprotic Acids with Strong Bases

Consider a volume V_o of a solution of a molecular polyprotic acid H_nA with overlapping ionisation steps of initial concentration C_o, which is titrated with a solution of strong base MOH of concentration C_B. The titration is assumed to be carried out in the acid range. In this range, the analysis of the titration curve leads to the following equation[19]

$$\hat{h} = \frac{\dfrac{K_1}{a_H\gamma_1} + \dfrac{2K_1K_2}{a_H^2\gamma_1} + \ldots + \dfrac{nK_1K_2\ldots K_n}{a_H^n\gamma_n}}{1 + \dfrac{K_1}{a_H\gamma_1} + \dfrac{K_1K_2}{a_H^2\gamma_1} + \ldots + \dfrac{K_1K_2\ldots K_n}{a_H^n\gamma_n}} \tag{32}$$

with

$$\hat{h} = \frac{[M^+] + [H^+] - [OH^-]}{C} \tag{33}$$

and

$$C = \frac{C_o V_o}{V_o + V} b_N C_o V_o = \frac{1}{n} b_N C_B V_e \ , \tag{34}$$

where γ_i denotes the activity coefficient of the species (i = 0, 1, 2, ..., n) and K_i the dissociation constants of the various ionisation steps.

For diprotic acids, Eq. (*32*) gives

$$y = -K_1 + K_1K_2\,x \tag{35}$$

with

$$y = \frac{Z}{X} \quad \text{and} \quad x = \frac{Y}{X} \tag{36}$$

and

$$\left.\begin{aligned} X &= \frac{\gamma_2\left[b_N C_B\left(V - \frac{V_e}{2}\right)\gamma_1 + a_H - \frac{K_w}{a_H}\right]a_H}{\gamma_1} \\ Y &= b_N C_B (V_e - V)\gamma_1 + \frac{K_w}{a_H} - a_H \\ Z &= \left(b_N C_B V\gamma_1 + a_H - \frac{K_w}{a_H}\right)a_H^2\gamma_2 \end{aligned}\right\} . \qquad (37)$$

For dilute solutions ($I < 10^{-1}$ M), the activity coefficients γ_1 and γ_2 can be determined from Eq. (*6*), and the ionic strength I of the solution from the following relationship[30]:

$$I = [M^+] + [H^+] + [A^{2-}] = b_N C_B V + \frac{a_H}{\gamma_1} + \left(\frac{K_1 K_2}{a_H^2 \gamma_2}\right)\frac{C}{D} , \qquad (38)$$

where

$$D = 1 + \frac{K_1}{a_H \gamma_1} + \frac{K_1 K_2}{a_H^2 \gamma_2} . \qquad (39)$$

The determination of V_e, K_1, and K_2 from Eq. (*35*), using V and pH data, is possible with the iterative method proposed here. It is assumed first that the value of V_e lies in an interval (a,b). Choosing arbitrarily from this interval a value for V_e, calculation of γ_1 and γ_2, at any point of the titration curve, requires of course the knowledge of the corresponding value of I. On the other hand, I is a function of K_1, K_2, γ_1, and γ_2. Thus, determination of γ_1 and γ_2 requires prior knowledge of γ_1 and γ_2. It appears that these calculations constitute a typical case of a vicious circle. However, γ_1 and γ_2 may be obtained by successive approximations. Assuming first that γ_1 and γ_2 equal 1, it is possible to determine approximate values (apparent constants) of K_1, K_2 from the coefficients of Eq. (*35*) using the experimental V and pH data.

Starting from these values and assuming again that γ_1 and γ_2 equal 1, so that $a_H = [H^+]$, it is possible to calculate I at any chosen point of the titration curve, and hence γ_1 and γ_2 from Eq. (*6*). These new values γ_1 and γ_2 can

be used to refine values of I and to repeat this until it converges (the criterion being less than the 10^{-5} difference in I between two subsequent cycles). By repeating these approximations at each point of the titration curve, it is possible to trace the curve $y = f(x)$ and to determine by the least-squares method the values of K_1 and K_2. These new values can be used to refine the values of K_1 and K_2 and to repeat this until they converge (the criterion being less than the 10^{-5} difference in pK_1 and pK_2 values between two subsequent cycles). The final curve $y = f(x)$, obtained using the approximation, approaches a straight line to the extent the chosen value of V_e also approaches the exact value of this parameter. Hence, the best linearity that could be obtained using the available experimental data evidently corresponds to the best approximation to the exact value of the equivalence volume. Therefore, by seeking within the interval (a,b) the V_e value, it is possible to trace N curves $y = f(x)$, N being the number of V_e values taken for these calculations. For each of these curves, the calculation of R_2 and S_{yx} permits the comparison of the adequacy of the fit of Eq. (*35*) to the experimental V and pH data. At the true value of V_e, these statistics may reach a maximum and a minimum value, respectively. Then, the exact values of K_1 and K_2 can be deduced, respectively, from the coefficients of the corresponding straight line.

An analogous procedure can be used in order to analyse the titration curve for triprotic acids. Indeed, in this case Eq. (*32*) gives

$$Y = K_1 + (K_1K_2)X_1 + (K_1K_2K_3)X_2 \qquad (40)$$

with

$$Y = \left(\frac{\hat{h}}{1-\hat{h}}\right)a_H\gamma_1, \quad X_1 = \left(\frac{2-\hat{h}}{1-\hat{h}}\right)\frac{\gamma_1}{a_H\gamma_2}, \quad X_2 = \left(\frac{3-\hat{h}}{1-\hat{h}}\right)\frac{\gamma_1}{a_H^2\gamma_3}. \qquad (41)$$

As previously, the activity coefficients γ_1, γ_2 and γ_3 can be determined from Eq. (*6*), where the ionic strength is given by the following formula[43]:

$$I = [M^+] + [H^+] + [HA^{2-}] + 3[A^{3-}] = \qquad (42)$$

$$= b_N C_B V + \frac{a_H}{\gamma_1} + \left(\frac{K_1K_2}{a_H^2\gamma_2} + \frac{K_1K_2K_3}{a_H^3\gamma_3}\right)\frac{C}{D},$$

where

$$D = 1 + \frac{K_1}{a_H \gamma_1} + \frac{K_1 K_2}{a_H^2 \gamma_2} + \frac{K_1 K_2 K_3}{a_H^3 \gamma_3} . \qquad (43)$$

The activity coefficients γ_1, γ_2, and γ_3 can be calculated by successive approximations, as described above.

The fact that Eq. (*40*) is linear, can be used for determination of V_e, K_1, K_2, and K_3, using the iterative method described in detail for monoprotic and diprotic acids.

2.5. Potentiometric Titration of Mixtures of Two Weak Diprotic Acids with Strong Bases

The titration of mixtures of two weak diprotic acids was also treated by Purdie *et al.* elsewhere[38]. However, the Purdie method requires the knowledge of the sum of the concentrations of the acids, the pK values being known. In contrast, in the present method the sum of the concentrations need not be known.

Consider a volume V_o of a mixture of two weak diprotic acids H_2A_1 and H_2A_2 of initial analytical concentrations C_1^o and C_2^o, which is titrated with a solution of a strong base MOH of concentration C_B. Assuming that all equally charged ions have the same activity coefficients, the dissociation constants K_{i1}, K_{i2} of the acid H_2A_i (with i = 1, 2) are given by

$$K_{i1} = \frac{a_H [HA_i^-] \gamma_1}{[H_2A_i]} , \quad K_{i2} = \frac{a_H [A_i^{2-}] \gamma_2}{[HA_i^-] \gamma_1} . \qquad (44)$$

At any point of the titration curve, a relatively simple calculation gives

$$Y = \left(\frac{K_{11}}{K_{21}} \right) C_1^o + C_2^o X , \qquad (45)$$

where

$$Y = \frac{F a_H^2 \gamma_1 \gamma_2 D_1}{b_N V_o (a_H \gamma_2 + 2K_{12} \gamma_1) K_{21}} , \quad X = \frac{D_1 (a_H \gamma_2 + 2K_{22} \gamma_1)}{D_2 (a_H \gamma_2 + 2K_{12} \gamma_1)} . \qquad (46)$$

and

$$D_i = 1 + \frac{K_{i1}}{a_H \gamma_1} + \frac{K_{i1} K_{i2}}{a_H^2 \gamma_2}, \qquad F = b_N C_B V + \frac{a_H}{\gamma_1} - \frac{K_w}{a_H \gamma_1}. \tag{47}$$

For dilute solutions ($I < 10^{-1}$ M), the activity coefficients γ_1 and γ_2 can be determined from Eq. (*6*). Concerning the ionic strength *I*, a simple calculation gives

$$I = [M^+] + [H^+] + [A_1^{2-}] + [A_2^{2-}] =$$

$$= b_N C_B V + \frac{a_H}{\gamma_1} + \frac{b_N V_o}{a_H^2 \gamma_2} \left(\frac{K_{11} K_{12} C_1^o}{D_1} + \frac{K_{21} K_{22} C_2^o}{D_2} \right). \tag{48}$$

Equation (*45*) predicts a linear relationship between *Y* and *X* with a *y*-intercept and slope equal to $(K_{11}/K_{21})C_1^o$ and C_2^o, respectively. Thus, the composition of the mixture can be deduced by linear regression from the coefficients of Eq. (*45*); the acidity constants K_{i1}, K_{i2} (with i = 1, 2) being known. This procedure can be realised by the presently proposed iterative method.

Assuming first that $I = b_N C_B V + a_H$, so that $a_H = [H^+]$ and $[A_1{}^{2-}]$, $[A_2{}^{2-}] \approx 0$, it is possible to determine, from the coefficients of Eq. (*45*) using the experimental *V* and pH data, approximate values of C_1^o and C_2^o. Starting from these values and assuming again that $a_H = [H^+]$, it is possible to calculate *I* from Eq. (*48*) at any chosen point of the titration curve, and hence γ_1 and γ_2 from Eq. (*6*). These new values of γ_1 and γ_2 can be used to refine values of *I* and to repeat this until it converges (the criterion being less than 10^{-5} difference in *I* between two subsequent cycles). By repeating these approximations at each point of the titration curve, it is possible to trace the curve $Y = f(X)$ and to determine by least-square method the values of C_1^o and C_2^o. These new values can be used to refine the values of C_1^o and C_2^o, and to repeat this until they converge (the criterion being less than the 10^{-12} difference in C_1^o and C_2^o values between two subsequent cycles).

2.6. Application of the Iterative Methods for the Analysis of Titration Curves

To establish the reliability of the proposed procedures, first it must be shown that they actually work by comparison with a system where the answer is already known. Experimentally, this implies that the proposed ap-

proaches, applied to previously reported systems, give reasonable (or even better) precision in extraction of the sought parameters. In this respect, it was considered necessary to test all the reported procedures: first, with simulated data corresponding to various values of the titration parameters and, second, with experimental titration data. These tests have revealed that the proposed techniques are fairly applicable[23,26].

Concerning the application of the iterative methods on simulated V and pH data, it has been found that the proposed techniques are able to extract V_e and pK values in the case where the simulated data are free of experimental errors ("ideal" data). However, more interesting from the experimental viewpoint is the question of how precisely the proposed methods are able to cope with data containing random extraneous contributions, such as the annoying experimental "noise". To investigate this, a Monte Carlo technique was used, as described in detail elsewhere[17]. The main idea of this procedure has been based on the observation that random experimental errors often closely follow a Gaussian (or normal) distribution. Thus, at each point (V_i and pH_i) of the "ideal" titration curve $pH_i = f(V_i)$, a number N of normally distributed random variables pH_{ij} with mean pH_i and standard deviation S_i were produced. At the experimental level this implies the realisation of N titrations with a precision equal to S_i. At each volume V_i, the obtained N values pH_{ij} were averaged. Evidently, the mean values $\langle pH_{ij} \rangle$ would coincide with the corresponding pH_i values only in the case where the number N of the produced random variables pH_{ij} tends to infinity. Using $\langle pH_{ij} \rangle$ data obtained for $N = 4$, it has been found that the proposed techniques lead with a fair accuracy (error <1%) to V_e and pK values, even when the simulated pH data are considerably obscured by extraneous noise ($S_i = 10^{-2}$ pH unit, namely 5–10 times greater than the accuracy of a precision instrument).

The proposed methods were also applied to various simulated titrations curves, corresponding to different pK values, where the pH data contained a systematic error equal to 10^{-2} pH unit. Experimentally, such errors are usually introduced by an erroneous standardization of the pH meter assembly. A systematic error in the pH values gives rise to relative titration errors δV_e and δpK in the values of V_e and pK, respectively, determined by $\delta V_e = (V_e - V_{e,syst})/V_e$ and $\delta pK = (pK - pK_{syst})/pK$, where $V_{e,syst}$ and pK_{syst} are the values of V_e and pK determined from data containing a systematic error equal to 10^{-2} pH unit. It has been found that δV_e and δpK depend on the strength of the acid that is being titrated. Also the variation of δV_e as a function of the acid strength presents a maximum in the immediate vicin-

ity of the pK value equal to 2.6 (ref.[23]). However, in all cases δV_e was less than 0.5%. Hence the proposed techniques are able to extract a V_e value with only a modest error, even when an important systematic error (δpH = 10^{-2} unit) obscures the pH data. It is worth noting that in the case of diprotic acids with pK_i > 2.9, the proposed techniques lead to the exact values of V_e even when the pH data contain an important systematic error equal to 2×10^{-2} pH unit. For these acids, a rough calibration of the electrode system is sufficient in order to extract the accurate value of the acid concentration. The titration error in the pK value decreases as pK increases. For moderately strong acids (with pK < 2.5) this error takes values greater than 1%, δpK being equal to 10^{-2}. In contrast, for acids with p$K \approx 4.8$ (such as the lower members of the series of aliphatic monocarboxylic acids) this error takes values equal to *ca* 0.2%. For such acids the proposed techniques are able to extract the V_e and pK values with only a modest error ($\delta V_e \approx$ 0.03% and δp$K \approx$ 0.2%), even when the pH data contain an important systematic error equal to 10^{-2} pH unit. Finally, for acids with pK > 3.8, it can be shown that the titration error in the pK values is approximately equal to the δpH error.

On the other hand, application of the iterative methods on experimental data leads to results that are very close to the corresponding data reported in the literature. As an example, we present here the application of the corresponding procedure on experimental data concerning the titration of a mixture of two weak monoprotic acids. This mixture was prepared by mixing 1.03×10^{-2} M propionic acid (30 ml) with 1.05×10^{-2} M formic acid (20 ml). The mixture was titrated with 1×10^{-1} M NaOH. As shown in Fig. 1a, the titration curve presents only one pronounced inflection (at $V \approx 5.18$ ml) corresponding to the total neutralisation of the mixture. The measurements carried out in the acidic range of the mixture are given in Table I.

It is now examined whether it is possible, using these data, to extract the desired pK and concentration values. In a first attempt R^2 *vs* V_e was varied: the starting value for C_1^o being 2×10^{-3} M; R^2 being a measure of the adequacy of the fit of Eq. (*29*) to the titrated data. The results obtained are presented graphically in Fig. 1b. It should be emphasised that one obtains identical results independently of the starting value for C_1^o.

Figure 1 shows that the graph $R^2 = f(V_e)$ presents a pronounced maximum in the vicinity of V_e = 5.2 ml. Further, for $5.08 \leq V_e \leq 5.28$, it was found that the curve $R^2 = f(V_e)$ can be perfectly fitted, by the least-square method, to the following polynomial (with the correlation coefficient better than 0.9995):

$$R^2 = \sum_{n=0}^{6} A_n V_e^n = -8.8752 + 5.3268V_e - 0.67377V_e^2 - \\ - 5.1405 \times 10^{-2} V_e^3 + 2.8774 \times 10^{-3} V_e^4 + \\ + 2.9221 \times 10^{-3} V_e^5 - 2.8269 \times 10^{-4} V_e^6 . \quad (49)$$

Consequently, the exact value of V_e, at which R^2 reaches maximum value, can be determined by solving (using any numerical method) Eq. (*50*).

$$\frac{dR^2}{dV_e} = 0 \quad (50)$$

The root of this equation was found equal to $V_e^{max} = 5.172$ ml ($C_{tot}^o = 1.034 \times 10^{-2}$ mol l^{-1}), which is the best approximation to the desired value of V_e.

In a second step, starting from this value of V_e, the variation of $\hat{C}_1^o$ with R_{cf} was examined. For 6.1×10^{-3} mol l$^{-1} \leq \hat{C}_1^o \leq 6.25 \times 10^{-3}$ mol l^{-1}, the following polynomial (with the square of the correlation coefficient very close to unity):

$$10^3 \hat{C}_1^o = 7.3866 - 3.7954R_{cf} + 4.9682R_{cf}^2 - 3.4283R_{cf}^3 + 1.2084R_{cf}^4 - 0.17165R_{cf}^5 . \quad (51)$$

TABLE I
Experimental titration data of an aqueous mixture of 1.029×10^{-2} M propionic acid (30 ml) and 1.051×10^{-2} M formic acid (20 ml) with 1×10^{-1} M NaOH at $T = 298.15$ K

V, ml	pH	*V*, ml	pH
1.00	3.639	2.59	4.432
1.17	3.727	2.84	4.545
1.31	3.800	3.04	4.638
1.48	3.888	3.20	4.710
1.65	3.975	3.35	4.778
1.80	4.050	3.52	4.860
1.97	4.133	3.67	4.932
2.12	4.207	3.87	5.036
2.27	4.278	4.01	5.107
2.42	4.348		

From this polynomial and for $R_{cf} = 1$ one obtains $\hat{C}_1^o = 6.168 \times 10^{-3}$ mol l^{-1}. This value is the best approximation to the exact value of C_1^o. Also it results that $C_2^o = C_{tot}^o - C_1^o = 4.176 \times 10^{-3}$ mol l^{-1}. These values are in excellent agreement with the expected values of C_1^o (= 30 × 0.1029/50 = 6.174×10^{-3} mol l^{-1}) and C_2^o (= 20 × 0.01051/50 = 4.204×10^{-3} mol l^{-1}). Finally, using the determined values of V_e and C_1^o, one obtains from the coefficients of Eq. (*23*) the values pK_1 = 4.877 and pK_2 = 3.742. These values are very close to the corresponding values (4.874 and 3.752, at 25 °C) reported in the literature[20,27].

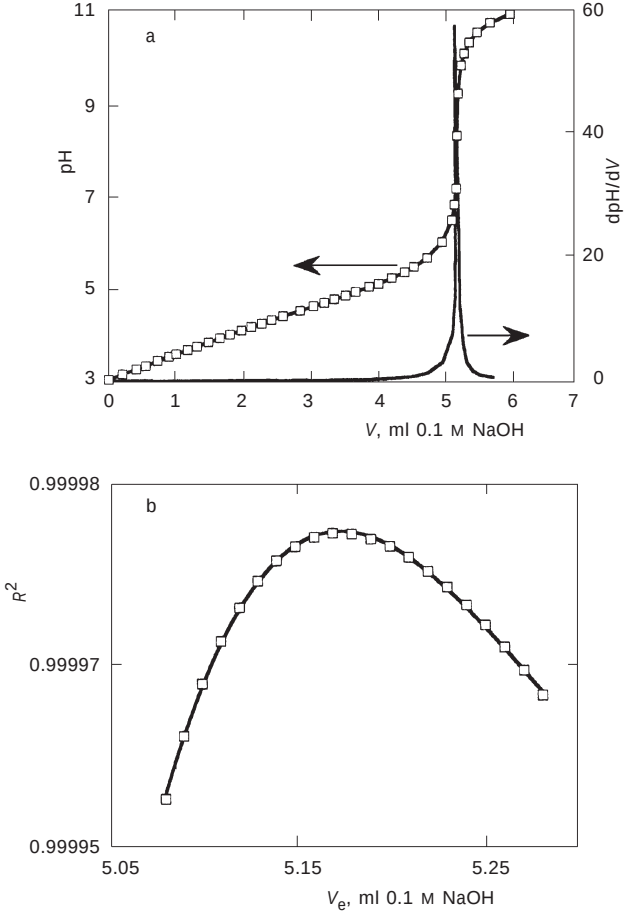


FIG. 1

Titration curve of an aqueous mixture of 1.029×10^{-2} M propionic acid (30 ml) and 1.051×10^{-2} M formic acid (20 ml) with 1×10^{-1} M NaOH (a), and variation of R^2 with V_e (b)

3. DETERMINATION OF KINETIC PARAMETERS FROM CHRONOAMPEROMETRIC DATA

3.1. Theoretical Background

Potential step chronoamperometry has proved to be a valuable technique for the study of various electrochemical reactions because of the relative simplicity of the mathematics involved in solving the appropriate diffusion equations. Some typical examples, for which the application of the above-mentioned technique leads to analytical solutions relating the current i with time t, are the reaction schemes (*I*)–(*V*).

$$\mathrm{A} \overset{n_1\mathrm{e}}{\rightleftharpoons} \mathrm{B} \xrightarrow{k_1} \mathrm{C} \overset{n_2\mathrm{e}}{\rightleftharpoons} \mathrm{D} \xrightarrow{k_2} \mathrm{E} \overset{n_3\mathrm{e}}{\rightleftharpoons} \mathrm{F} \qquad (I)$$

$$\mathrm{A} \overset{n_1\mathrm{e}}{\rightleftharpoons} \mathrm{B} \xrightarrow{k_1} \mathrm{C} \overset{n_2\mathrm{e}}{\rightleftharpoons} \mathrm{D} \qquad (II)$$

$$\mathrm{O} + n\mathrm{e} \overset{k_\mathrm{f}}{\rightleftharpoons} \mathrm{R} \qquad (III)$$

$$\mathrm{O} + n\mathrm{e} \underset{k_\mathrm{b}}{\overset{k_\mathrm{f}}{\rightleftharpoons}} \mathrm{R} \qquad (IV)$$

$$\mathrm{O} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{P} \overset{n\mathrm{e}}{\underset{\text{fast}}{\rightleftharpoons}} \mathrm{R} \qquad (V)$$

The theoretical treatment of the so-called ECECE mechanism (reaction scheme (*I*)) for potential step chronoamperometry at a planar electrode, the initial and boundary value problems, treated by means of the Laplace transform method, led to the following relation[16]:

$$\frac{i}{n_1 FAD^{1/2} c_\mathrm{A}^\mathrm{b}} = \left(1 + \frac{n_2}{n_1}\Phi_1(t) + \frac{n_3}{n_1}\Phi_2(t)\right)\frac{1}{\sqrt{\pi t}}, \qquad (52)$$

where c_A^b is the bulk concentration of species A, F is Faraday constant, A is the electrode area, and D is the assumed common diffusion coefficient of all the species involved in the ECECE sequence. The functions $\Phi_1(t)$ and $\Phi_2(t)$ are defined by the relations:

$$\Phi_1(t) = 1 - e^{-k_1 t}$$

$$\Phi_2(t) = 1 - e^{-k_1 t} - \frac{\sqrt{t}}{2} \exp\left(-\frac{k_1 + k_2}{2} t\right) X(t), \tag{53}$$

where

$$X(t) = \int_0^t \frac{(1 - e^{-k_1 y}) \exp\left(\frac{k_1 + k_2}{2} y\right)}{y^{3/2}} I_0\left(\frac{k_1 - k_2}{2}(t - y)\right) dy \tag{54}$$

and $I_0(x)$ is the modified Bessel function of zero order, x being the argument $\{(k_1 - k_2)/2\}(t - y)$.

For the ECE mechanism (reaction scheme (*II*), the current–time relation is given by (ref.[14]):

$$\frac{i}{n_1 F A D^{1/2} c_A^b} = \left(1 + \frac{n_2}{n_1}(1 - e^{-kt})\right) \frac{1}{\sqrt{\pi t}}. \tag{55}$$

The chronoamperometric relations for the reaction schemes (*III*) (irreversible mechanism), (*IV*) (quasi-reversible mechanism) and (*V*) (CE mechanism) have the respective forms[14]

$$i = nFAc_o^b k_f \exp(\beta_1^2 t) \operatorname{erfc}(\beta_1 \sqrt{t}) \tag{56}$$

$$i = nFAc_o^b k_f \exp(\beta_2^2 t) \operatorname{erfc}(\beta_2 \sqrt{t}) \tag{57}$$

$$i = nF\beta_3 c_o^b A\sqrt{D} \exp(\beta_3^2 t) \operatorname{erfc}(\beta_3 \sqrt{t}), \tag{58}$$

where $\beta_1 = k_f/\sqrt{D}$, $\beta_2 = (k_f + k_b)/\sqrt{D}$, $\beta_3 = k_1/\sqrt{k_{-1}}$, provided that $k_{-1} >> k_1$, and D is the assumed common diffusion coefficient of all the species involved in reaction schemes (*III*)–(*V*).

The reaction schemes (*III*)–(*V*) share a chronoamperometric response of the form

$$i = i_o \exp(\beta^2 t) \operatorname{erfc}(\beta\sqrt{t}), \tag{59}$$

where i_o is the initial current, usually not accessible by direct measurement.

Equation (*52*) can be applied for studying the kinetics of homogeneous chemical reactions involved in the ECECE mechanism. However, because of its non-linear form, the determination of the rate constants from $i = f(t)$ curves using classic numerical methods appears to be very difficult. That was the reason why in a previous investigation[16] we chose alternative methods for the determination of the rate constants of the intervening chemical reactions in the ECECE mechanism of 1,4-benzoquinone dioxime (*p*-BQD). Nevertheless, it is not always possible to find such alternative methods for determining the rate constants in any ECECE mechanism.

Equation (*59*) also has a non-linear form. Thus, the determination of the corresponding rate constants from $i = f(t)$ plots by using traditional numerical methods without prior knowledge of A, D or i_0 appears to be very difficult. For this reason, various approximate methods for the determination of the rate constants have been suggested in the literature[44–48]. These methods, using either disc or ring-disc measurements, or chronoamperometric data at short or long times, allow to evaluate the kinetic parameters with only low precision. Of course, there exist numerical methods that can extract from Eq. (*59*) the accurate values of the corresponding kinetic parameter[14,49]. However, these methods (based on the linearisation of the chronoamperometric data either in Laplace space or by calculating the semi-integral of the current) are of a complexity that does not appeal to the average chemist. An alternative technique to these methods has been devised in the literature[50]. However, this procedure is of experimental complexity, since it requires combination of chronoamperometric and chronocoulometric data.

This situation has encouraged us to develop new iterative methods, based on Eqs (*52*), (*55*), and (*59*) that allow determination of the exact values for the corresponding rate constants exclusively from chronoamperometric data[15–17].

3.2. Determination of the Rate Constants k_1 and k_2 of an ECECE Mechanism

This method is based on the main principles of a previous one[31,51] that was used for the determination of the rate constants for two competitive parallel reactions preceded by an equilibrium between two of the reactants.

Equation (*52*) can be rearranged to give the following form:

$$Y = bX \,, \qquad (60)$$

where

$$Y = \frac{i\sqrt{t}}{n_1 FAD^{1/2} c_A^b}, \quad X = 1 + \frac{n_2}{n_1}\Phi_1(t) + \frac{n_3}{n_1}\Phi_2(t). \qquad (61)$$

Equation (*60*) predicts a linear relationship between Y and X with a gradient equal to $1/\sqrt{\pi}$. Alternatively, the experimental confirmation of such a correlation supports the assumption that the reduction under consideration does, in fact, follow an ECECE mechanism.

However, despite the fact that plots of Y *vs* X offer a theoretical basis for the correlation of the results, their practical application may be regarded as fairly limited. Indeed, calculation of X at various times requires estimates of k_1 and k_2 that are generally not available.

However, as mentioned above, approximate values of these constants could be obtained in certain instances by alternative methods. We examine now whether it is possible, starting from these values, to determine the exact k_1 and k_2 values, using only experimental chronoamperometric data.

We assume first that the values of k_1 and k_2, *a priori* accessible, are defined by a set S including an infinity of elements. Each element of S corresponds to a pair of values of k_1 and k_2. Consequently, the various elements of S define various electrochemical reactions following the ECECE mechanism. Using an element of S (namely a pair of k_1 and k_2 values chosen arbitrarily), it is possible to trace, using the chronoamperometric data, the curve $Y = f(X)$. This will approach a straight line to the extent where the chosen values of the rate constants also approach the exact k_1 and k_2 values. Thus, the best linearity that could be obtained, using the available experimental data, corresponds evidently to the best approximation to the exact values of the sought rate constants.

However, among infinity of elements of S, there is of course one corresponding to the electrochemical reaction under consideration. In an attempt to determine the values of the rate constants corresponding to this element, we assume that we have an initial estimation of either k_1 or k_2. Let k_1^o be an approximate value of k_1. This value can be obtained by an alternative method. Starting from this value, it is possible to trace N curves $Y = f(X)$, N being the number of k_2 values taken for these calculations. For each of these curves, the calculation of the squared correlation coefficient R^2 allows to compare the linearity of the various $Y = f(X)$ plots and to trace the curve $R^2 = f(k_2)$. This curve is expected to reach a pronounced maximum at a value of k_2 equal to k_2^1, which can be considered as a first approximation to the exact k_2 value.

In a second step, starting from k_2^1, it is possible to trace the curve $R^2 = f(k_1)$ and to determine, in the same way, the first approximation k_1^1 to the k_1 value.

This procedure can be repeated n times in order to obtain the sequences $\{k_1^n\}$ and $\{k_2^n\}$ that converge to the limiting values $k_1^{\lim}$ and $k_2^{\lim}$, expressing the best approximation to the exact values of the corresponding rate constants. It should be noted that as n grows, k_2^1 and k_2^n are expected to be increasingly better estimates of the desired rate constants. One stops the iterations when sufficient accuracy is obtained.

3.3. Determination of the Rate Constants of ECE, Irreversible, Quasi-Reversible, and CE Mechanisms

Equations (*55*) and (*59*) can be written as

$$y = Bx\,, \tag{62}$$

where (for Eq. (*55*))

$$y = \frac{i\sqrt{\pi t}}{n_1 F c_A^b}\,, \quad x = 1 + \frac{n_2}{n_1}(1 - e^{-kt})\,, \quad B = A\sqrt{D} \tag{63}$$

(for Eq. (*59*))

$$y = i\,, \quad x = \exp(\beta^2 t)\,\mathrm{erfc}(\beta\sqrt{t})\,, \quad B = i_o\,. \tag{64}$$

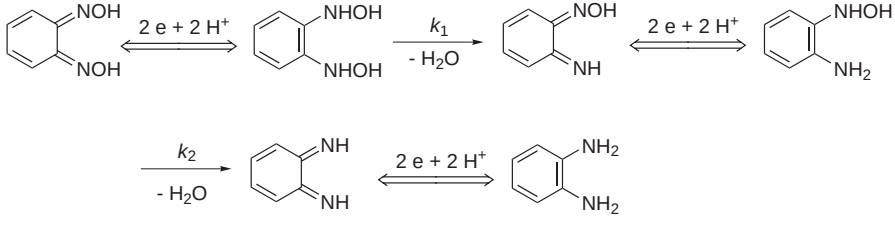
Equation (*62*) predicts a linear relationship between y and x. As in the case of the ECECE mechanism, the experimental confirmation of such a correlation, using the above equations, supports the assumption that the reaction under consideration follows, indeed, the corresponding mechanism. However, there is no way in which, without prior knowledge of the kinetic parameters, the *y vs x* plots give a linear graph. This is possible with the proposed iterative method.

We assume first that the value of the corresponding kinetic parameter k' (k' denoting k or β) lies in an interval (a,b). Choosing arbitrarily from this interval a value for k', it is possible to trace, using the chronoamperometric data, the curve $y = f(x)$. This will approach a straight line to the extent where the chosen value for k' also approaches the exact value of the corresponding kinetic parameter. Thus, the best linearity that could be obtained,

using the available experimental data, corresponds evidently to the best approximation to the exact value of k'. Hence, by seeking within the interval (a,b) the k' value, it is possible to trace N curves $y = f(x)$, N being the number of k' values taken for these calculations. For each of these curves, the calculation of the squared correlation coefficient R^2 allows to compare the linearity of various $y = f(x)$ plots and trace the curve $R^2 = f(k')$. This curve is expected to present a pronounced maximum at a value of k' equal to k'_{max}, which can be considered as the best approximation to the exact value of the kinetic parameter. The slope of the straight line corresponding to k'_{max} is the best approximation to the exact value of B (being equal to $A\sqrt{D}$ or i_o).

3.4. Application of the Iterative Methods for Determination of Kinetic Parameters from Chronoamperometric Data

All the methods described herein were applied to simulated chronoamperometric data, either without or with extraneous "noise" (Monte Carlo simulated data), for different values of the corresponding kinetic parameters[15,17]. The Monte Carlo data were produced as described previously in the case of the analysis of titration data. The obtained results showed that these procedures are able to extract the kinetic parameters with only modest errors, even when the faradaic data are considerably obscured by random extraneous contributions, such as annoying experimental "noise". The reported techniques were also successfully applied to experimental data[15,17]. As an example, we present here the determination of k_1 and k_2 of an ECECE mechanism, using experimental data concerning the reduction of 1,2-benzoquinone dioxime (10^{-3} M) in aqueous 5×10^{-1} M $HClO_4$ and 2.5×10^{-4} M $Bi(ClO_4)_3$ solution at a Pt electrode modified by underpotential deposition (upd) of Bi at 25 °C. The reduction of 1,2-benzoquinone dioxime (*o*-BQD) at a Pt/Bi(upd) modified electrodes in acidic solutions proceeds *via* the mechanism shown in Scheme 1 [18].



SCHEME 1

Mean values of i obtained from three independent experiments are given in Table II. The values of Y calculated from Eq. (*61*) are also listed in Table II. In these calculations, the effective (real) electrode area A and the diffusion coefficient D were taken equal to 0.136 cm^2 and 6.80×10^{-6} cm^2 s^{-1}, respectively[52]. Using the values of Y reported in Table II, the following smoothing function was found by the least-square method ($R^2 > 0.9993$):

$$Y = 0.65249 + 10.786t - 69.413t^2 + 259.55t^3 - 497.54t^4 + 375.53t^5 \quad (65)$$

Smoothed Y values (Y_{sm}), calculated from Eq. (*65*), were used in the application of the iterative procedure for the determination of the rate constants k_1 and k_2. It is noted that the Y_{sm} values, used in the iterations, ranged from

TABLE II
Experimental current values for the reduction of *o*-BQD at a Pt/Bi(upd) electrode in aqueous acid solutions and the values of Y calculated from Eq. (*61*) at T = 298.15 K

t, s	i, μA	Y
0.05	320.39	1.04615
0.08	287.72	1.18834
0.10	271.05	1.25164
0.13	251.01	1.32157
0.15	239.62	1.35517
0.18	227.51	1.40952
0.20	220.27	1.43845
0.23	209.48	1.46704
0.25	204.47	1.49289
0.28	195.52	1.51079
0.30	191.70	1.53322
0.33	184.48	1.54751
0.35	180.63	1.56042
0.38	174.77	1.57322
0.40	170.99	1.57917

0.05 to 0.35 s, since in this region the process under consideration shows a pronounced kinetic character.

The rate constants of the coupled chemical reactions could be determined exclusively from chronoamperometric data (the iterative method reaches the exact values of k_1 and k_2 even if one starts from very poor estimates of either k_1 or k_2). However, approximate values at least for one rate constant should be useful, since the number of iterations required is smaller when the starting value is closer to its real magnitude. For this reason, the approximate value k_1 = 26.14 s^{-1}, determined previously[18], was used as the starting value of the iterative technique. The $\{k_1^n\}$ and $\{k_2^n\}$ sequences are summarised in Table III. It should be noted that in all cases the variations $R^2 = f(k_j)$ (with j = 1 or 2) showed pronounced maxima, such as plotted in Fig. 2a.

As can be deduced from Table III, one practically reaches the desired values after six iterations. The mean value obtained (for $n > 6$) was equal to k_1^n = 28.25 ± 0.01 s^{-1} and k_2^n = 7.488 ± 0.003 s^{-1}. The small fluctuations observed around the limiting values for $n > 6$ can be attributed to round-off

TABLE III
Successive approximations to k_1 and k_2 values obtained by the iterative method for an ECECE mechanism and using the experimental data reported in Table II. T = 298.15 K

n	k_1^n, s^{-1}	k_2^n, s^{-1}
0	26.14	
1	26.738	6.185
2	27.411	6.621
3	27.892	7.065
4	28.126	7.331
5	28.210	7.437
6	28.239	7.474
7	28.249	7.484
8	28.247	7.489
9	28.254	7.487
10	28.258	7.490
11	28.246	7.492

errors, introduced mainly in the determination of the maxima of the $R^2 = f(k_j)$ curves.

To test the exactness of the values derived using Eq. (*52*), the curve $i = f(t)$ was traced and compared with experimental i values. The agreement is excellent (Fig. 2b).

On the other hand, the determination of X as a function of t, using Eq. (*61*) and the values for k_1 and k_2 extracted above, allows to correlate the variation of Y with X. This variation was found to be perfectly linear, the

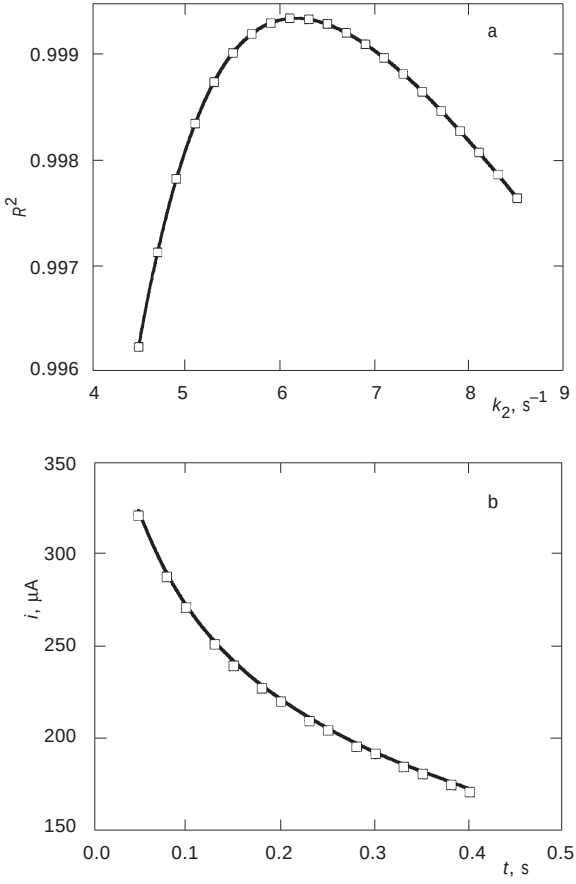


FIG. 2

Chronoamperometric response for the reduction of *o*-BQD at a Pt/Bi(upd) electrode in aqueous acid solution. Variation of R^2 with k_2 ($k_1 = k_1^\circ = 26.14$ s^{-1}) (a), and variation of the current with time (b). Theoretical curve calculated using $k_1 = 28.25$ s^{-1} and $k_2 = 7.488$ s^{-1} (—), experimental values (❑)

corresponding correlation coefficient being very close to unity. The slope b of this dependence, found equal to 0.5611, is very close to the theoretical one ($b = 1/\sqrt{\pi} = 0.5642$). This behaviour provides further experimental evidence that the reduction of *o*-BQD at a Pt/Bi(upd) electrode proceeds *via* an ECECE mechanism.

4. CONCLUSIONS

Theory and iterative methods for analysis of potentiometric titration data are presented in this paper. The proposed methods, using equations derived without approximations, and data exclusively resulting from the buffer region of a titration curve, enable the prediction of the accurate values of the concentration(s) and the thermodynamic dissociation constant(s) of the titrated acid(s), even if the titration is stopped well before the end-point of the titration. All these methods can successfully be applied in titrations without any sharp end-point, or for the determination of the analytical concentration and the thermodynamic pK value for a moderately weak acid in the presence of other very weak acids, the neutralisation of which is undesirable. The last determination can easily be done by stopping the titration well before the end-point. The majority of the methods reported in the literature are valid when (i) the titrations are carried out under conditions of constant ionic strength, and (ii) the accurate value of the analytical concentration of the titrated acid is known. On the contrary, the proposed procedures described above are valid even when (i) the titrations are performed under conditions of varying ionic strength (but, there is no reason why the analysis would not be carried out under conditions of constant ionic strength), and (ii) the accurate value of the analytical concentration of the titrated acid is not known. Hence, the addition of a neutral salt to the titrated solution to keep the ionic strength constant, is not necessary. Therefore, the pK values obtained in media of a low ionic strength are free of any possible “salt effect”. Another advantage of the proposed techniques, in comparison to other approaches in the literature, is the simultaneous determination of the accurate values of the analytical concentration and the corresponding thermodynamic pK value of the titrated acid. Indeed, thermodynamic pK values being independent of the concentration could be considered as the “fingerprint” of the titrated acid. Thus, from the comparison of the determined pK values with the tabulated ones it is possible to identify the titrated acid.

Iterative methods for evaluating the chronoamperometric curves of various electrochemical mechanisms are proposed. Thus, in the case of an

ECECE mechanism, the proposed method allows to determine the exact values of the corresponding rate constants k_1 and k_2. The test of this procedure, using simulated ideal data (free of any extraneous "noise"), showed that this method is fairly well applicable. Application of the iterative technique to Monte Carlo simulated data revealed that the proposed procedure is also able to extract kinetic parameters even if the faradaic data are considerably obscured by "noise". Finally, this method was successfully applied to experimental chronoamperometric data.

The proposed method for the analysis of chronoamperometric data of various electrochemical mechanisms (ECE, irreversible, quasi-reversible, and CE mechanisms) is also applicable even if the faradaic data are considerably obscured by gaussian "noise". The main advantage of this iterative method, in comparison with other methods currently in use, is that the accurate values of the rate constants of the coupled chemical reactions in the CE and ECE mechanisms can be obtained directly from the *i–t* data even if the parameters *A* (the effective electrode area) and *D* are not known. These parameters are usually not available.

5. REFERENCES

1. Thompson H., Svehla G.: *Microchem. J.* **1968**, *13*, 576.
2. Bontchev P. R.: *Talanta* **1972**, *19*, 675.
3. Otto M., Muller H., Werner G.: *Talanta* **1978**, *25*, 123.
4. Dickson E. L., Svehla G.: *Microchem. J.* **1979**, *24*, 509.
5. Yurist I. M., Talmud M. M., Zaitsev D. M.: *Zh. Anal. Khim.* **1985**, *40*, 1157.
6. Alekseeva I. I., Chernysheva L. M., Bobkova M. V., Solomonov V. A.: *Zh. Anal. Khim.* **1987**, *42*, 362.
7. Mathers F. C., Kuebler J. R.: *Trans. Am. Electrochem. Soc.* **1916**, *29*, 417.
8. Fuseya G., Murata K.: *Trans. Am. Electrochem. Soc.* **1926**, *L(1)*, 235.
9. Vladmirova V. F.: *Sb. Nauchn. Soobshch. Dagest. Gos. Univ., Kafedra Khim.* **1969**, *5*, 55.
10. Carlos I. A., Souza C. A. C., Pallone E. M. J. A., Francisco R. H. P., Cardoso V., Lima-Neto B. S.: *J. Appl. Electrochem.* **2000**, *30*, 987.
11. Amblard J., Froment M., Georgoulis K., Papanastasiou G.: *Surf. Technol.* **1978**, *6*, 409.
12. Papanastasiou G., Jannakoudakis D., Amblard J., Froment M.: *J. Appl. Electrochem.* **1985**, *15*, 71.
13. Zarkadas G. M., Stergiou A., Papanastasiou G.: *J. Appl. Electrochem.* **2001**, *31*, 1251.
14. Macdonald D. D.: *Transient Techniques in Electrochemistry*, p. 57. Plenum Press, New York 1981.
15. Papanastasiou G., Kokkinidis G., Papadopoulos N.: *J. Electroanal. Chem.* **1993**, *352*, 153.
16. Kokkinidis G., Papanastasiou G.: *J. Electroanal. Chem.* **1988**, *257*, 239.
17. Papanastasiou G., Kokkinidis G., Papadopoulos N.: *J. Electroanal. Chem.* **1991**, *305*, 19.
18. Kokkinidis G., Papanastasiou G., Hasiotis C., Papadopoulos N.: *J. Electroanal. Chem.* **1991**, *309*, 263.
19. King E.: *The International Encyclopedia of Physical Chemistry, Chemical Physics. Acid-Base Equilibria*, 1st ed., Vol. 4, pp. 64, 83, 227. Pergamon Press, Oxford 1965.

20. Albert A., Serjeant E. P.: *The Determination of Ionization Constants*, 2nd ed., pp. 9, 84. Chapman & Hall Ltd, London 1971.
21. Harris D. C.: *Quantitative Chemical Analysis*, 5th ed., p. 239. Freeman & Co., New York 1999.
22. Prue J. E.: *The International Encyclopedia of Physical Chemistry, Chemical Physics. Ionic Equilibria*, 1st ed., Vol. 3, p. 6. Pergamon Press, Oxford 1966.
23. Papanastasiou G., Ziogas I., Kokkinidis G.: *Anal. Chim. Acta* **1993**, *277*, 119.
24. Grunwald E.: *J. Am. Chem. Soc.* **1951**, *73*, 4934.
25. Freiser H., Fernando Q.: *Ionic Equilibria in Analytical Chemistry*, p. 240. John Wiley, New York 1966.
26. Papanastasiou G., Ziogas I.: *Talanta* **1995**, *42*, 827.
27. Robinson R. A., Stokes R. H.: *Electrolyte Solutions*, 2nd ed., pp. 230, 517. Butterworths, London 1968.
28. Bacarella A. L., Grunwald E., Marshall H. P., Purlee E. L.: *J. Org. Chem.* **1955**, *20*, 747.
29. De Ligny C. L., Luykx P. F. M., Rehbach M., Wieneke A. A.: *Rec. Trav. Chim.* **1960**, *79*, 713.
30. Papanastasiou G., Stalidis G., Jannakoudakis D.: *Bull. Soc. Chim. Fr. I* **1984**, 255.
31. Cayzergues P., Georgoulis C., Papanastasiou G.: *J. Chim. Phys.* **1977**, *74*, 1112.
32. Papanastasiou G., Papoutsis A., Jannakoudakis D., Georgoulis C.: *J. Chim. Phys.* **1985**, *83*, 907.
33. Papoutsis A., Papanastasiou G., Jannakoudakis D., Georgoulis C.: *J. Chim. Phys.* **1985**, *83*, 913.
34. Papanastasiou G., Papoutsis A., Tsirtou M., Ziogas I.: *J. Solution Chem.* **1996**, *25*, 203.
35. Johanson A.: *Talanta* **1970**, *95*, 535.
36. Pehrson L., Ingman F., Johanson S.: *Talanta* **1976**, *23*, 781.
37. Frisque A., Meloche V. W.: *Anal. Chem.* **1954**, *26*, 468.
38. Purdie N., Tomson M. B., Cook G. K.: *Anal. Chem.* **1972**, *44*, 1525.
39. Kankare J. J.: *Anal. Chem.* **1973**, *45*, 1877.
40. Ingman F., Johanson A., Johanson S., Karlsson R.: *Anal. Chim. Acta* **1973**, *64*, 113.
41. Ivaska A.: *Talanta* **1974**, *21*, 1167.
42. Ivaska A.: *Talanta* **1975**, *22*, 995.
43. Papanastasiou G., Ziogas I.: *Talanta* **1989**, *36*, 977.
44. Malachesky P. A., Marcoux L. S., Adams R. N.: *J. Phys. Chem.* **1966**, *70*, 4068.
45. Filinovsky V. Y.: *Elektrokhimiya* **1969**, *5*, 635.
46. Galus Z.: *Fundamentals of Electrochemical Analysis*, p. 187. Ellis Harwood, Chichester 1976.
47. Jonson C. A., Barnartt S.: *J. Electrochem. Soc.* **1967**, *114*, 1256.
48. Prater K. G., Bard A. J.: *J. Electrochem. Soc.* **1970**, *117*, 1517.
49. Oldham K. B.: *J. Electroanal. Chem.* **1983**, *145*, 9.
50. Barbero C., Zon M. A., Fernandez H.: *J. Electroanal. Chem.* **1989**, *265*, 23.
51. Cayzergues P., Georgoulis C., Papanastasiou G.: *C. R. Acad. Sci. Paris, Ser. C* **1977**, *285*, 163.
52. Kokkinidis G., Argyropoulos N.: *Electrochim. Acta* **1985**, *30*, 1611.