

Control of the electrochemical reduction of *o*-nitrophenol by pH imposition in acetonitrile

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Abstract

An electrochemical study using d.c. polarography, cyclic voltammetry and coulometry of *o*-nitrophenol has been performed in acetonitrile, in the presence of five buffer solutions of pH 20.0, 17.2, 16.2, 11.8 and 8.1. Using linear sweep voltammetry, it was found that at pH 20, the mechanism involves a reversible monoelectronic charge transfer in an E_r mechanism. This is possible by avoiding the self-protonation reaction. At lower pH values, the mechanism involves a reversible monoelectronic charge transfer followed by protonation steps and homogeneous charge transfer due to disproportionation of the protonated intermediates. At pH 17.2 and 11.8, the mechanisms for the homogeneous charge transfer steps were found to be of DISP2 type (disproportionation order two). At pH 16.2 and 8.1, mechanisms of the DISP1 or ECE type (disproportionation order one) are proposed. Coulometry experiments support the mechanisms proposed: at pH 20, $\text{O}\phi\text{NO}_2 + 1e^- = \text{O}\phi\text{NO}_2^-$; at pH 17.2, $\text{HO}\phi\text{NO}_2 + 2e^- + \text{H}^+ = \text{HO}\phi\text{NO}_2\text{H}^-$; at pH 16.2, $\text{HO}\phi\text{NO}_2 + 2e^- + 2\text{H}^+ = \text{HO}\phi\text{NO} + \text{H}_2\text{O}$; at pH 11.8, $\text{HO}\phi\text{NO}_2 + 3e^- + 3\text{H}^+ = \text{HO}\phi\text{NOH} + \text{H}_2\text{O}$; and at pH 8.1, $\text{HO}\phi\text{NO}_2 + 4e^- + 4\text{H}^+ = \text{HO}\phi\text{NHOH} + \text{H}_2\text{O}$. From polarographic $I/I_0 = f(\text{pH})$ plots, it was possible to assign $\text{p}K_a$ values to the acid–base pairs involved. © 1997 Elsevier Science S.A.

Keywords: *o*-Nitrophenol; pH; Reduction; Electrochemistry; Acetonitrile

1. Introduction

The electroreduction of nitroderivatives, particularly nitroarenes, is of great importance since their several reduction products are key compounds in preparative organic synthesis [1]. Besides, a large group of nitroderivatives possess pharmaceutical properties determined strongly by their redox–pH behavior [2,3].

Several papers have been published showing that the electroreduction of nitroarenes is of a multielectronic nature, involving a series of intermediates of anionic radical type which present a basic character and great reactivity towards proton donors present in the reaction medium, with the solvent itself, or even with protons present in the molecule by means of self-protonation reactions [4]. Then, the redox behavior is related closely to their acid–base properties, whose strength depends on their structure and

on the acidity level of the solution. Therefore it is very important to study the influence of the pH of the reaction medium.

This influence has been studied by Laviron and Roullier [5] in pH buffered solution using water as solvent, since in this medium the preparation and control of pH buffer solutions are very well established. Savéant and coworkers [4] have published the electroreduction of *o*-nitrophenol in DMSO without buffering. They report that the first reduction peak of *o*-nitrophenol is chemically irreversible at low sweep rates and the 6e⁻ hydroxyphenylamino derivative is obtained together with the conjugate base of the starting material, $\text{O}\phi\text{NO}_2^-$, in a ratio 1:6 due to the uncontrolled autoprotonation reaction.

The effect of proton donors on the reduction of aromatic nitro compounds in aprotic solvents has been examined by Chambers and coworkers [6]; they observed that the one-electron reversible reduction wave, which occurs in the absence of a proton donor, is shifted to more positive potentials when different acids are added to the medium, and this shift can be correlated approximately

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with the relative strength of the proton donor. However, a complete explanation is not reported in their work. Hoytink [7] reported a similar effect, with water as proton donor, in the polarographic reduction of anthracene which, under non-aqueous conditions, presents two reversible one-electron waves. When the water content increases, the first wave grows at the expense of the second wave, corresponding to the gradual protonation of the electrogenerated anion radical. Karajus and Zuman [8] have reported the electroreduction of several aromatic and heterocyclic nitro compounds, but not *o*-nitrophenols, in buffered mixtures of water and DMF, but they refer the pH of the reaction medium to that of aqueous buffer before mixing with the aprotic solvent.

The necessity of working with buffered media in pure aprotic solvents in order to establish the relative predominance of the proton transfer chemical reaction coupled to the electroreduction of organic compounds has been pointed out by Andrieux et al. [9] since 1975 when they proposed a solution of 2% H₂O in acetonitrile (AN) as a buffered medium; however, nothing was established concerning the acidity level of the reaction medium. Then, to the best of our knowledge, there are no electrochemical studies of the electroreduction of *o*-nitrophenol in acetonitrile or any other solvent in several buffer solutions of known pH.

The electrochemical behavior of nitrophenols is compatible with the scheme of a series of consecutive reactions involving proton and electron exchange in order to produce the corresponding reduced derivatives. Depending on the medium and the nature of the nitrophenol, the reduction mechanism can be either of the ECE type or a disproportionation reaction of the type DISP1 or DISP2 [10].

Recently, we have reported [11] that the electroreduction of a natural quinone can be controlled by pH if suitable buffer solutions in pure acetonitrile are employed. Indeed, at pH 17.2 a DISP2 type mechanism is observed and at pH 15.5 a DISP1 type is established.

In this work, a study of the reduction mechanism of *o*-nitrophenol was performed in acetonitrile as the aprotic medium in the presence of five different buffer solutions in this solvent, in order to show that acidity levels determine the type of mechanism of the reduction of this nitrophenol as a typical nitroarene compound. Linear sweep voltammetry, d.c. polarography and some coulometric techniques were employed to show the change in mechanism of electroreduction with the pH of the medium.

2. Experimental

Pure (AR grade) *o*-nitrophenol was used. Acetonitrile (AR grade) dried with phosphorus pentoxide and distilled over molecular sieves was used as solvent. The supporting electrolyte was tetrabutylammonium perchlorate (TBAP, reagent grade), dried at 90°C overnight before use. A

HMDE of about 0.0029 cm² surface area was used as the working electrode for voltammetric experiments. Two solid electrodes were used as working electrodes for coulometric studies: a polished platinum disk microelectrode of about 0.031 cm² surface area, and a platinum ultramicroelectrode of about 10 μm diameter according to Baranski et al. [12]. For polarographic determinations a DME was used (*t* = 1 s). Exhaustive coulometry was performed with a Hg⁰ pool of about 1 cm² as the working electrode. A silver wire immersed in a solution of 0.01 M in AgNO₃ and 0.1 M TBAP in acetonitrile was used as the reference electrode [13]. The potentials reported in this work are referred to the ferrocene/ferricinium couple according to IUPAC recommendations [14]. In our case, $E(\text{Fc}/\text{Fc}^+) = 0.040 \text{ V vs. } E(\text{Ag}/\text{Ag}^+)$. The cell was maintained in a pure nitrogen atmosphere at all times. Voltammograms were recorded on an XY plotter and chronoamperometric measurements were performed with a DEI digital electrochemical analyzer (Radiometer-Tacussel). The coulometric and polarographic experiments were performed with the latter equipment as well. The diffusion coefficient required for the calculation of the non-dimensional cathodic current functions [10] $\Psi = I/FScD^{1/2}(Fv/RT)^{1/2}$ was taken as $D = 5.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, a value typical of this kind of compound in AN [12].

The heterogenous buffer solution was prepared by mixing 0.5 mmol of conjugate base and the corresponding acid added from a 0.1 M stock solution in AN. Solid bases and acids were previously dried overnight. The following acid–base pairs were employed: sodium benzoate ↓ (NaBz ↓); benzoic acid/sodium benzoate ↓ (HBz/NaBz); salicylic acid/sodium bisalicylate ↓ (H₂Sal/NaHSal); oxalic acid/sodium oxalate ↓ (HOx/Na₂Ox); methanesulfonic acid/sodium methanesulfonate ↓ (HMet/NaMet). A 20 mM stock solution of *o*-nitrophenol was prepared in AN.

The pH value of the above solutions was determined by means of previous calibration of the glass electrode as reported by Kolthoff and Chantooni [15], according to the spectrophotometric method using *o*-nitroaniline as indicator and measuring the absorption of the yellow at 410 nm. The absorption of *o*-aniline alone, A_0 , and mixed with several aliquots of 0.5 M anhydrous perchloric acid, A_i , was measured to determine the pH of the calibration curve and buffer solutions, both in 0.1 M TBAP in AN, according to

$$\text{pH} = 4.85 + \log \frac{A_i}{A_0 - A_i}$$

where 4.85 is the p*K* value of *o*-nitroanilinium/*o*-nitroaniline in the solutions employed. The e.m.f. measurements were performed between the glass electrode and the same reference electrode used for the electrochemical studies described above.

3. Results and discussion

For the glass electrode used in this study, the calibration plot of pH vs. e.m.f. in millivolts yields a straight line with a slope of 56.3 mV, in good agreement with those reported in the literature [15]. An equation obtained by means of linear regression analysis of the calibration plot data was used to determine the pH of the buffer solutions employed:

$$E = 605 - 56.3\text{pH} \quad (r^2 = 0.9916)$$

This equation refers to our glass electrode.

Fig. 1 shows the voltammetric behavior, at 400 mV s^{-1} , of *o*-nitrophenol (1 mM) on the HMDE in 0.1 M TBAP in AN in three different buffer solutions: (a) NaBz↓ (NaBBS) pH 20; (b) HBz/NaBz (BBS) pH 17.2; (c) H₂Sal/NaHSal (SBS) pH 15.5.

From Fig. 1(a), pH 20, it is observed that *o*-nitrophenol presents a reduction peak at a large negative potential and an oxidation peak in the reverse scan, with $(I_p^a/I_p^c) \cong 1$. The latter behavior suggests a reversible reduction. Since at pH 20 a neutralizing base is present, the acidic hydrogen of the *o*-phenol cannot act as an inner proton donor in a typical autoprotonation reaction [4], since it is already neutralized. To support the latter result, the $\text{p}K_a$ of the acid–base conjugate pair $\text{HO}\phi\text{NO}_2/\text{O}^-\phi\text{NO}_2$ was determined spectrophotometrically according to Freiser and coworkers [16] by measuring the absorbance of the yellow at 390 nm of a $50 \mu\text{M}$ *o*-nitrophenol solution in 0.1 M TBAP in AN in the range $20 < \text{pH} < 8$ in buffered media; a $\text{p}K_a$ of 19.0 was found. Thus, at pH 20 (NaBBS) *o*-nitrophenol is practically deprotonated in solution.

From Fig. 1(b) and Fig. 1(c) it is observed that at pH 17.2 (BBS) and pH 15.5 (SBS) an increment of the cathodic peak occurs. Fig. 2 shows the current function $I_p/v^{1/2}$ for the reduction peak in the above reaction medium. It is observed that the current function is constant at high scan rates. Thus, the electrochemical process is controlled by diffusion [17]. Under these conditions the values are approximately twice as great at pH 17.2 and 15.5 as at pH 20. This is an indication that the electron

transfer number in BBS and SBS is twice as great as that at pH 20 (NaBBS).

3.1. Determination of the number of electrons

In order to determine the number n of electrons involved in the reversible reduction of *o*-nitrophenol at pH 20, coulometric studies were performed by three different methods.

The first, according to Baranski et al. [12], is based on the chronoamperometric value of I_{∞} with an ultramicroelectrode and the slope S of the plot $I = f(t^{-1/2})$ obtained with a disk microelectrode. Instead of the HMDE (used for the voltammetric study), solid electrodes were used in this method. Both chronoamperograms are obtained in this work by imposing a fixed potential at the corresponding Pt electrodes. The current value is measured at a sufficiently long time to assure a steady state value. Under such conditions, the current is proportional to n . The number of electrons is obtained according to the relationship

$$\frac{n}{n_{\text{std}}} = \frac{S^2 I_{\infty(\text{std})} c_{\text{std}}}{S_{\text{std}}^2 I_{\infty} c}$$

where the subscript std refers to the parameters of a compound used as a standard. In this work, solutions of pure ferrocene in 0.1 M TBAP in AN were used as standards. The number n of electrons was determined using five solutions of the standard in the range $1 \text{ mM} < c_{\text{std}} < 5 \text{ mM}$, and five solutions of *o*-nitrophenol in the same range of concentration. A value of $n = 1.2 \pm 0.15$ was found.

In order to corroborate the value obtained above, a second coulometric method was used. According to Heyrovský [18], the number of electrons can be obtained from the slope of the straight line $\log I_{\text{lim}} = f(t)$ during the drop growth of the polarographic DME at E_{imp} . The reduction of 2 ml of 2.75 mM *o*-nitrophenol in 0.1 M TBAP in AN and NaBBS pH 20 at $E_{\text{imp}} = -2.1 \text{ V}$ yields $n = 0.8$ from the slope of the straight line obtained ($r^2 > 0.99$).

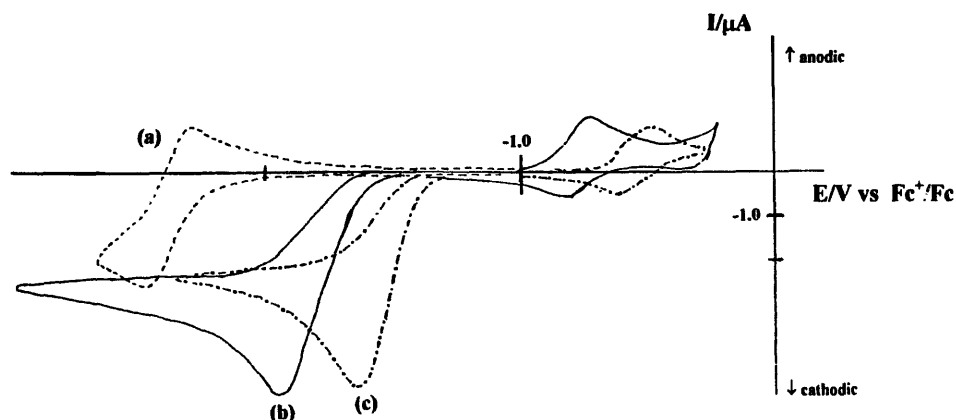


Fig. 1. Voltammetric, $v = 400 \text{ mV s}^{-1}$, behavior of *o*-nitrophenol (1 mM) at the HMDE in 0.1 M TBAP in acetonitrile in three buffer solutions: (a) sodium benzoate ↓ (NaBBS) pH 20; (b) benzoic/benzoate (HBz/NaBz ↓) buffer solution (BBS) pH 17.2; (c) salicylic acid/bisalicylate (H₂Sal/NaHSal ↓) buffer solution (SBS) pH 15.5.

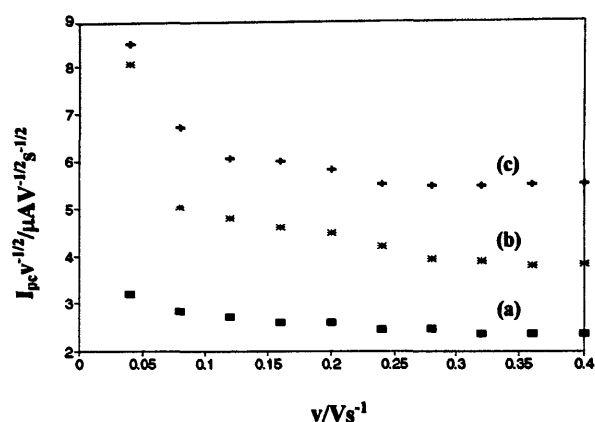


Fig. 2. Variation of the current function of the reduction of 1 mM *o*-nitrophenol at the HMDE with sweep potential in 0.1 M TBAP in acetonitrile in different buffer solutions: (a) sodium benzoate ↓ (NaBBS) pH 20; (b) benzoic/benzoate (HBz/NaBz ↓) buffer solution (BBS) pH 17.2; (c) salicylic acid/bisalicylate (H₂Sal/NaHSal ↓) buffer solution (SBS) pH 15.5.

Exhaustive coulometry with a Hg⁰ pool of about 1 cm² yields a value of $n = 1.2$ when 2 ml of 2 mM *o*-nitrophenol in 0.1 M TBAP in AN and NaBSS pH 20 was electrolyzed at $E_{\text{imp}} = -2.1$ V. The quantity of electricity was obtained by integration of the chronoamperogram obtained.

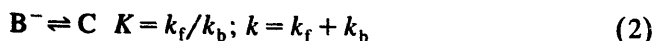
At pH 17.2, $n = 2.3$ by exhaustive coulometry and $n = 1.87$ by the polarographic method, supporting the results obtained above by voltammetry.

By exhaustive coulometry with a Hg⁰ pool as described above, the following results were obtained: at pH 16.2, $n = 1.98$; at pH 11.8, $n = 2.9$; and at pH 8.1, $n = 4.3$.

The results obtained by cyclic voltammetry and coulometry show that it is possible to establish the reduction pathway by fixing the acidity level of the reaction medium. It is possible to get different reduction intermediates according to the pH of the medium, since the number of electrons needed for the reduction depends on the chosen acidity level of the reaction medium.

3.2. Determination of the mechanism type

Even though voltammetric and coulometric experiments indicate changes in mechanism with changing acidity levels of the reaction medium, more quantitative evidence is needed in order to define and differentiate the trajectory of the reaction. Indeed, these reactions could be protonation reactions involved in an ECE mechanism [19,20] or else in DISP1 and DISP2 mechanisms [10], as in the case of aromatic hydrocarbons



where reactions (2) and (5) may be proton transfer reactions and (4) may be a homogeneous charge transfer reaction.

Sequences:

Reactions (1), (2), (3)

⇒ ECE mechanism, slow step is (2)

Reactions (1), (2), (4)

⇒ DISP1 mechanism, slow step is (2)

Reactions (1), (2), (4)

⇒ DISP2 mechanism, slow step is (4)

The above scheme accounts for the first two electron exchanges, which may explain the results obtained at pH > 15 where $n = 2$ is found. Nevertheless, this first reduction pattern may be repeated for a higher number of electrons exchanged, this pattern being the limiting step in the whole reduction process.

First of all, the non-dimensional cathodic current functions $\Psi_p = I_p / FScD^{1/2}(Fv/RT)^{1/2}$ for pH values 20.0, 17.2, 16.2 and 11.8 were calculated. The Ψ values were calculated with I_p taken at a scan rate of 400 mV s⁻¹ since $I_p/v^{1/2}$ was practically constant from 250 mV s⁻¹. Previously, current values obtained on the HMDE were corrected for the spherical contribution $I_{\text{sph}} = nFSDc\phi(\sigma t)/r_0$ using $\phi(\sigma t)$ values from the literature [21] to obtain current values for planar diffusion. Experimental non-dimensional values Ψ_{exp} are compared with those reported in the literature for several situations [10]:

pH 20.0	$\Psi_{\text{exp}} < \Psi_{\text{diff}} < \Psi_{\text{ECE-DISP1}} < \Psi_{\text{DISP2}}$
	$0.46 < 0.466 < 0.992 < 1.054$
pH 17.2	$\Psi_{\text{diff}} < \Psi_{\text{ECE-DISP1}} < \Psi_{\text{exp}} < \Psi_{\text{DISP2}}$
	$0.466 < 0.992 < 1.01 < 1.054$
pH 16.2	$\Psi_{\text{diff}} < \Psi_{\text{exp}} < \Psi_{\text{ECE-DISP1}} < \Psi_{\text{DISP2}}$
	$0.466 < 0.70 < 0.992 < 1.054$
pH 11.8	$\Psi_{\text{diff}} < \Psi_{\text{ECE-DISP1}} < \Psi_{\text{DISP2}} < \Psi_{\text{exp}}$
	$0.466 < 0.992 < 1.054 < 1.18$

It can be noted that the experimental non-dimensional current function Ψ_{exp} at pH 20 approaches that of Ψ_{diff} , which corresponds to a one-electron transfer under diffusion control (E_r mechanism). This result is in good agreement with the above results.

At both pH 17.2 and 11.8, Ψ_{exp} values approach that of Ψ_{DISP2} where more than one electron is involved. At pH 16.2 the value of the experimental non-dimensional current function approaches that of $\Psi_{\text{ECE-DISP1}}$ given by a mechanism ECE-DISP1 (under pure kinetic conditions, i.e. an irreversible peak).

Since the current function does not vary very significantly between them, attention was focused on the peak potential E_p variations. E_p vs. $\log v$ (v = scan rate) is obtained for 1 mM *o*-nitrophenol in the different buffer solutions. At pH 20 the linear tendency of the experimental

points ($r^2 > 0.9$) shows no variation (slope value 0.00) in E_p vs. $\log v$. This linear tendency of the experimental points ($r^2 > 0.9$) shows a smaller slope for the pH 17.2 values (0.019 V/decade) than that obtained for the pH 16.2 values (0.025 V/decade). Theoretical values 0.03 V/decade for ECE-DISP1 and 0.02 V/decade for DISP2 mechanisms are reported [10,22]. In addition, it was found that the behavior E_p vs. $\log c$ is linear ($r^2 > 0.9$) at the pH studied, yielding a slope of 0.001 at pH 20, a slope of 0.032 V/decade at pH 17.2 and a slope of 0.003 V/decade at pH 15.5. Theoretical values reported are 0.020 V/decade for DISP2 (disproportionation order two) and 0.000 V for ECE-DISP1 and E_r (disproportionation order one and pure diffusion mechanisms respectively).

According to the latter results the mechanism changes from a reversible one-electron reduction at pH 20 to a DISP2 one at pH 17.2 where the homogeneous charge transfer reaction (4) determines the mechanism (disproportionation order two). At pH 16.2 the mechanism changes again to a DISP1 one. The pH is low enough for the reaction (2) (acid–base reaction) to determine the whole mechanism. These results are in very good agreement with those found with the quinone-type natural product hormone reported previously by the authors [11].

At pH 11.84 E_p vs. $\log c$ presents a slope value of 0.034 V/decade that indicates a DISP2 mechanism, but E_p vs. $\log v$ presents a slope value of 0.034 V/decade which is high for this mechanism, and a number $n = 3$ of electrons exchanged. The latter behavior can be attributed to a transition region according to this kind of voltammetric study [10].

The coulometric and voltammetric analyses indicate the presence of acid–base intermediates whose relative acid–base strength contributes to determining the type of mechanism. This strength is given by the buffer solutions employed to establish the mechanism.

DISP1 and DISP2 mechanisms suppose that the disproportionation reaction is irreversible. Usually this occurs because one of its products undergoes a fast protonation reaction. Modification of pH allows the control of the protonation reactions that involve the products of the disproportionation reaction. In the time window of the voltammetric studies performed, the protonation reactions were detected as fast ($I_p/v^{1/2}$ functions are independent of scan rate).

3.3. Polarographic determination of the pK'_a of the intermediates

In order to support the voltammetric and coulometric results obtained above and to obtain more quantitative information about the mechanisms proposed above, a polarographic study was performed. For the pK'_a determinations, a DME was used. At pH 20 a single one-electron wave was observed for the first reduction of *o*-nitrophenol. Fig. 3 shows the increment of the first polarographic

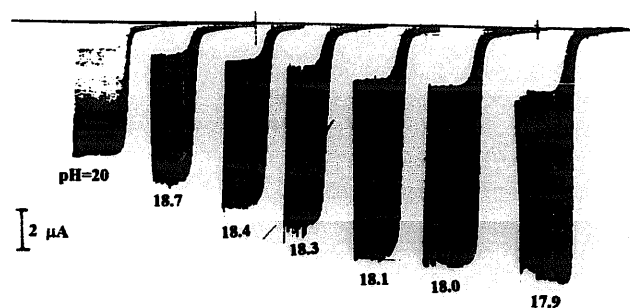


Fig. 3. Typical d.c. polarographic curves of 1 mM *o*-nitrophenol in 0.1 M TBAP alkaline buffered solutions (BBS) in acetonitrile obtained at a DME with dropping time 2 s. An increment of I_{lim} with decreasing pH is observed. For the case shown in this figure, the buffer solutions are formed by adding benzoic acid aliquots to (NaBBS) pH 20.

limiting current I from the one-electron limiting current I_0 when the pH is decreased with BBS mixtures. Fig. 4 shows the pH dependence of the relative current I/I_0 of the first wave reduction of 1 mM *o*-nitrophenol in 0.1 M TBAP in AN and several buffered solutions in the pH range $8.6 < \text{pH} < 20$. From this figure it is observed that the shape of the plots obtained corresponds to a dissociation curve according to [23]

$$\frac{I}{I_0} = \frac{0.886\sqrt{(k_r t_1 / K_a)} [H^+]}{1 + 0.886\sqrt{(k_r t_1 / K_a)} [H^+]}$$

where I is the mean limiting current measured at a given value of $[H^+]$, I_0 is the limiting current at pH 20 (corresponding to the one-electron wave), K_a the thermodynamic dissociation constant for the protonated species produced at the electrode, k_r is the rate constant of the protonation of the same species, and t_1 is the drop time. The plot $I/I_0 = f(\text{pH})$ is characterized by inflection points occurring at a pH value that can be denoted by pK'_a associated with the acid–base pairs involved in the reduction process. From Fig. 4 the successive values of pK'_a found were: 18, 16, 12 and 8 approximately.

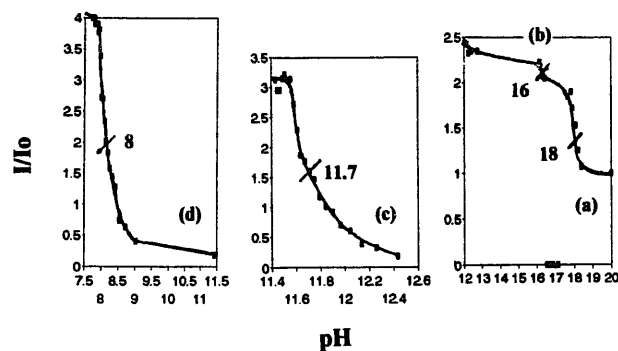


Fig. 4. pH dependence of the relative current I/I_0 (shown in Fig. 3) of the first wave reduction of 1 mM *o*-nitrophenol in 0.1 M TBAP in AN and several buffered solutions (BBS). The pK'_a values are indicated for each wave. The buffer solutions were formed by adding: (a) benzoic acid aliquots to NaBBS, pH 20; (b) salicylic acid to NaHSal, pH 16.5; (c) oxalic acid to NaOx, pH 12.5; and (d) methanesulfonic acid to NaMet, pH 11.5.

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