PULSE POLAROGRAPHIC STUDY OF THE BEHAVIOUR OF SOME *o,o'*-DIHYDROXYAZO-COMPOUNDS

Enric CASASSAS*, Miquel ESTEBAN and Santiago ALIER**

Departament de Química Analítica, Universitat de Barcelona,
Av. Diagonal 647, 08028 Barcelona, Spain

The reduction of several *o,o'*-dihydroxyazo-compounds is studied by means of pulse polarographic techniques (DPP, NPP and RPP). The compounds studied are the following: 2-(2'-hydroxyphenylazo)-phenol (*o,o'*-dihydroxyazobenzene), 1-(2'-hydroxy-1'-naphthylazo)-2-naphthol-4--sulphonic acid (calcon or Eriochrome Blue Black R), 1-(2'-hydroxy-4'-sulpho-1'-naphthylazo)--2-hydroxy-3-naphthoic acid (calcon carboxylic acid), and 1-(1'-hydroxy-2'-naphthylazo)-6--nitro-2-naphthol-4-sulphonic acid (Eriochrome Black T). Correlations between I_p and E_p and experimental variables (pH, T, conc.) and instrumental parameters (dropping time, t, and pulse magnitude, ΔE) are established.

Reaction mechanisms formerly proposed are discussed on the basis of the new obtained results, and the ranges are defined where adsorption and/or acid-base catalysis are operative.

Azo dyes which have two donor groups *ortho* to the azo linkage, like the *o,o'*-dihydroxyazo dyes, are powerful chelating agents[1] and some of them have found application as metallochromic indicators[2]. Florence et al.[3-5] showed that the polarographic reduction of azocompounds containing strongly electron-releasing substituent groups (such as –OH and –SO₃H, present in the compounds studied here) yields unstable hydrazo intermediates and proceeds directly to the amine stage, giving a single 4-electron wave. When the azocompound contains a strongly electron-attracting substituent (as –NO₂) the hydrazo intermediates are relatively stable in acidic medium and two polarographic 2-electron waves are obtained. Furthermore, the reduction of a NO₂-containing azocompound is a base-catalyzed process.

In the present work the reduction processes of the following *o,o'*-dihydroxy-substituted azocompounds are studied: 2-(2'-hydroxyphenylazo)-phenol (or *o,o'*-dihydroxyazobenzene) (*I*); 1-(2'-hydroxy-1'-naphthylazo)-2-naphthol-4-sulphonic acid (or Calcon, or Eriochrome Blue Black R) (*II*) (C.I. Nr. 15 705); 1-(2'-hydroxy-4'--sulpho-1'-naphthylazo)-2-hydroxy-3-naphthoic acid (or Calcon carboxylic acid) (*III*) and 1-(1'-hydroxy-2'-naphthylazo)-6-nitro-2-naphthol-4-sulphonic acid (or

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Eriochrome Black T) (*IV*) (C.I. Nr. 14 645). Pulse polarography in its different forms differential (DPP), normal (NPP) and reverse (RPP) are employed.
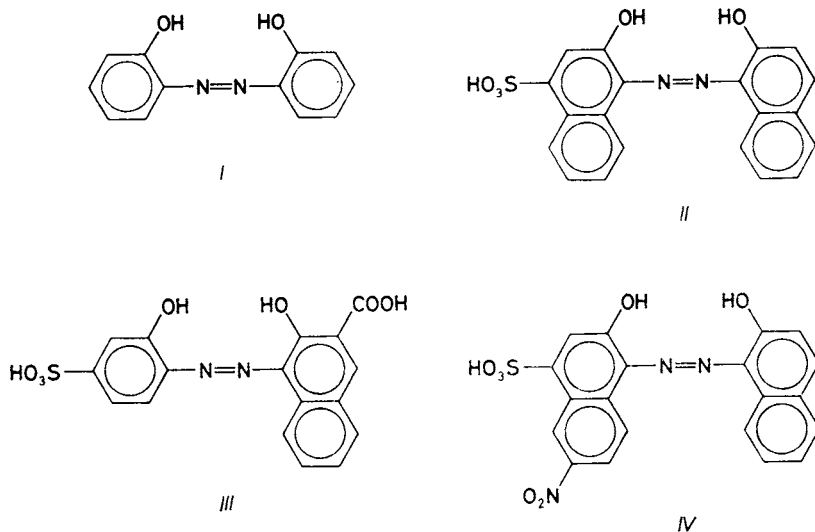
EXPERIMENTAL

Apparatus

Pulse polarograph Tacussel PRG-5 attached to a X–Y recorder Varian F-100. Reference electrode was a SCE, working electrode a DME ($m^{2/3}t^{1/6} = 4.71 \pm 0.02$ mg$^{2/3}$s$^{1/6}$, 0.1 mol l^{-1} KCl solution, between 0.2 and −0.6 V, 30 cm mercury head column) regulated by a Tacussel hammer Model MP-03 (± 0.1 s precision). Auxiliary electrode was a platinum wire electrode. pH-meter Radiometer PHM-26.

Reagents

Reagents used for buffer preparation were Merck, a.r., except HCl (UCB, a.r.). Azocompounds were Merck (used without further purification) except *o,o'*-dihydroxyazobenzene (Eastman––Kodak, purified as described[6]).

Solutions

Buffer solutions, according to Clark and Lubs[7], from pH 1 to 7; according to Bates and Bower[8] from pH 7 to 11·5. Azocompounds stock solutions, daily prepared in order to avoid molecular aggregation[9,10]. Eriochrome Black T and Calcon carboxylic acid stock solutions are $1 . 10^{-4}$ mol. . l^{-1} aqueous solutions, those of *o,o'*-dihydroxyazobenzene (in ethanol) and Calcon (in water) are $1 . 10^{-2}$ mol l^{-1}. Working solutions are prepared by dilution in the aqueous buffer solutions.

RESULTS

At pH < 5.0 the *o,o'*-dihydroxyazobenzene yields only one DPP peak; at pH > 5.0 its peak height, I_p, strongly decreases, while a new smaller peak appears at less cathodic potentials. At pH > 10.50, the more cathodic peak becomes predominant. At pH 7.0, both peaks show a I_p vs $t^{2/3}$ linear variation, with an intercept equal to zero for the less cathodic peak and different from zero for the other one.

Calcon yields at pH < 7.0 only one reduction DPP peak; at pH > 8.0 a second, more cathodic, peak is observed. At pH values between 7 and 10.4 a third more negative peak, at about -1.06 V, is present. The sum of peak heights is constant, with the second peak as the highest one. Both I_p values for the peak appearing in acidic medium (pH 4.0) and the first peak obtained in basic medium (pH 9.05) vary non-linearly with $t^{2/3}$, whereas both the second and third peaks appearing in basic medium (pH 9) show linearity. The plot of I_p vs $t^{2/3}$ for the second basic peak fails to pass through the origin. No linear relationships I_p vs $(1 - \sigma)/(1 + \sigma)$ are obtained, not even at low scan rates. In all cases the plots E_p vs ΔE are linear with slope values of c. 0.5. In ammonia–ammonium chloride buffer solutions (pH 10), only two peaks are formed, at -0.6 V and -1.2 V, and the intermediate peak at about -0.9 V present in other buffer solutions does not appear. The first one is a well defined peak and its height changes with the solution age.

Calcon carboxylic acid behaves similarly to calcon in acidic and weakly basic solutions, although the peak towards -1.06 V does not appear. At pH between 9.5 and 10.5, DPP shows two peaks; the height of the first one (the one which pre-exists in acidic media) strongly decreases with increasing pH, while the height of the second more negative peak steadily increases. At pH > 10.5 this one becomes the unique polarographic signal. Only this peak in basic medium (pH > 9.0) shows a linear correlation I_p vs $t^{2/3}$, with an intercept different from zero.

Eriochrome Black T solutions at pH < 5.5 give DPP curves showing two peaks of about the same height. At pH > 5.5 and up to pH 9, the more cathodic peak drastically decreases in height. From pH 9 to 13 there is only one peak present, whose height is equal to the sum of peak heights appearing in acidic solutions. In more basic media (pH > 13), two peaks appear again. In ammonia–ammonium chloride buffer solutions the second peak which characterizes the more basic solutions begins to appear at a lower pH (c. 10). The peak appearing at the intermediate basic media (pH 8.6) shows a linear plot of I_p vs $t^{2/3}$, with an intercept different from zero, but for the peaks in acidic medium (pH 4.6) the variation is not linear.

Table I summarizes some of the polarographic results just described. Table II shows the relationships of I_p and E_p vs conc., obtained by DPP for all the studied compounds. In all cases, linear plots of E_p vs pH are obtained, with slope values in the range -50 to -60 mV/pH unit.

In general, the NPP waves of the azocompounds obtained for different media show high maxima, at slightly more negative values than their $E_{1/2}$, while the RPP

waves are well defined (Fig. 1). For Eriochrome Black T some distorted RPP curves are obtained at neutral pH (pH 6·5), which partially overlap at acidic medium. The comparison of the limiting currents for both techniques does not show uniform results as regards the signal, the compound and the pH.

TABLE I

Pulse polarographic parameters of several o,o'-dihydroxyazo compounds at several pH; 25°C

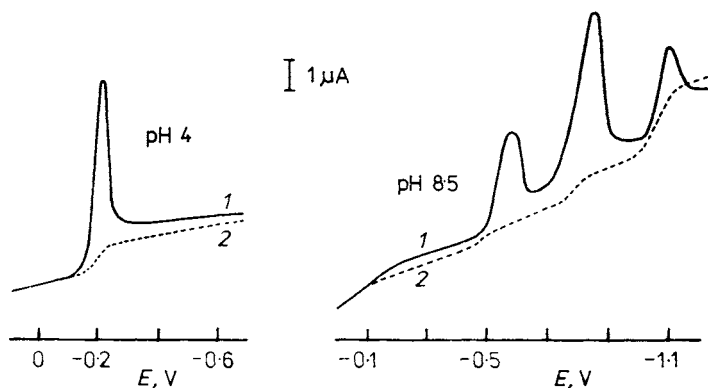| Compound	pH	First peak		Second peak		Third peak	
		I_p, μA	E_p, V	I_p, μA	E_p, V	I_p, μA	E_p, V
o,o'-Dihydroxyazobenzene	7·3	0·016	−0·303	0·071	−0·412	—	—
Calcon	4·0	0·277	−0·165	—	—	—	—
	9·0	0·075	−0·540	0·067	−0·944	0·085	−1·024
Calcon carboxylic acid	3·9	1·433	−0·172	—	—	—	—
	8·3	1·040	−0·490			—	—
Eriochrome black T	4·0	0·297	−0·218	0·233	−0·272	—	—
	8·5	1·228	−0·526	—	—	—	—

FIG. 1

Normal (1) and reverse (2) pulse polarograms of calcon at different pH values. $2 . 10^{-5}$ mol l^{-1}, $t = 2$ s and $v = 2$ mV s^{-1}

TABLE II

Relationships of peak heights and peak potentials of several o,o'-dihydroxyazo compounds with their concentrations

Compound	c, mol l^{-1}	pH	I_p (μA) vs c (mol l^{-1})	r^2	E_p, V
o,o'-Dihydroxyazobenzene	$8 . 10^{-6} - 1 \cdot 4 . 10^{-5}$	7·30	$I_{p_1} = 3 \cdot 61 . 10^{-4} + 1 \cdot 85 . 10^3 c$	0·9984	$-0 \cdot 305$
			$I_{p_2} = 4 \cdot 97 . 10^{-2} + 1 \cdot 71 . 10^3 c$	0·9897	$-0 \cdot 417$
Calcon	$1 . 10^{-5} - 3 \cdot 8 . 10^{-5}$	4·01	$I_{p_1} = 2 \cdot 51 . 10^{-2} + 1 \cdot 23 . 10^4 c$	0·9896	$-0 \cdot 166$
		9·05	$I_{p_1} = 5 \cdot 28 . 10^{-2} + 1 \cdot 15 . 10^3 c$	0·9938	$-0 \cdot 536$
			$I_{p_2} = 9 \cdot 94 . 10^{-3} + 4 \cdot 21 . 10^3 c$	0·9993	$-0 \cdot 960 \rightarrow 0 \cdot 925^a$
			$I_{p_3} = 1 \cdot 25 . 10^{-2} + 5 \cdot 25 . 10^3 c$	0·9985	$-1 \cdot 010 \rightarrow 1 \cdot 045$
Calcon carboxylic acid	$2 . 10^{-5} - 1 . 10^{-4}$	4·05	$I_{p_1} = 2 \cdot 68 . 10^{-2} + 2 \cdot 34 . 10^4 c$	0·9878	$-0 \cdot 125$
		9·10	$I_{p_1} = 7 \cdot 18 . 10^{-2} + 1 \cdot 34 . 10^4 c$	0·9962	$-0 \cdot 498$
Eriochrome black T	$2 . 10^{-5} - 1 . 10^{-4}$	4·08	$I_{p_1} = 4 \cdot 13 . 10^{-2} + 4 \cdot 25 . 10^3 c$	0·9819	$-0 \cdot 185$
			$I_{p_2} = 2 \cdot 48 . 10^{-2} + 3 \cdot 77 . 10^3 c$	0·9861	$-0 \cdot 247$
		9·60	$I_{p_1} = 8 \cdot 06 . 10^{-2} + 2 \cdot 07 . 10^4 c$	0·9973	$-0 \cdot 596$

^{a} E_p varies with concentration according to: $E_{p_2} = -0 \cdot 676 + 0 \cdot 056 \log c$, $r^2 = 0 \cdot 9869$; $E_{p_3} = -1 \cdot 307 - 0 \cdot 059 \log c$, $r^2 = 0 \cdot 9968$.

DISCUSSION

The polarographic behaviour of the o,o'-dihydroxyazocompounds studied is rather complex, and several features are observed that are not common to all of these compounds. The mechanism proposed by Florence[3] is valid in general, but a detailed interpretation of the characteristic behaviour of each of the compounds studied requires further discussion.

o,o'-Dihydroxyazobenzene

The observed E_p vs pH relationships and the high I_p values at pH < 5 and pH > 10 obtained by DPP agree with the Florence's assumption of the acid-catalyzed and the base-catalyzed, respectively, reduction of the azocompound directly to the amine stage. In the intermediate pH range the reduction is uncatalyzed and its kinetics is very much slower. The protons consumed are supplied by diffusion from the bulk of the buffer solution. Noticeable adsorption phenomena must exist, even at low concentration levels $(10^{-5} \text{ mol } l^{-1})$, because the linear I_p vs $t^{2/3}$ plot does not pass through the origin.

Calcon

In acidic medium only one well-defined polarographic peak is produced, which implies a transfer of four electrons and four protons per molecule[3-5]. In basic medium the non linear i_p vs $(1 - \sigma)/(1 + \sigma)$ relationships show not fully reversible behaviour[11]. This behaviour, together with the appearance of two peaks at -0.536 V and at c. -0.94 V is attributed[12] to adsorption, following a non-linear isotherm of the type discussed by Flanagan et al.[13]. The appearance of high maxima by NPP but not by RPP can be explained on the basis of reactant adsorption, as observed for p-nitrophenol[14] and for polyelectrolytic systems[15]. The application of the normalized peak current criterium according to Anson et al.[16] is not conclusive. The third more cathodic peak appearing in basic media can be perhaps related to the protonation state of the species being reduced on the electrode, which would catalyze the electroreduction of water. It is not possible, therefore, to propose a simple mechanism for calcon reduction in basic medium, because of the intervening processes of adsorption, molecular aggreagtion and catalytic hydrogen discharge. The two peaks obtained in ammonia–ammonium buffer should correspond to the reduction of the non-protonated and protonated forms of the azocompound, and the medium favours the process with lesser adsorption at the electrode[17].

Calcon Carboxylic Acid

One of the distinguishing features in the behaviour of calcon carboxylic acid is the change in peak height. Analogously to the mechanism proposed for the polaro-

graphic reduction of methyl red[18], which is based on an orientation change in the adsorbed molecule, the present results can be interpreted also on the basis of a change in the orientation of the plane of calcon carboxylic acid molecules with respect to the electrode surface on which they are adsorbed. Within the pH range where two forms can co-exist (protonated and unprotonated *o*- and *o'*-hydroxyl groups) two polarographic peaks are observed, probably due to the different adsorption isotherms of these forms. For non linear isotherms two DPP peaks can be expected[13]. At pH > 11 both hydroxyl and carboxyl groups are unprotonated and the two orientations responsible for the two peaks cease to exist. In all cases the overall process is the direct reduction of the azo group to the amine. The presence of reactant adsorption phenomena is proved by the curves obtained by NPP and RPP, as it was shown for calcon.

Eriochrome Black T

In acidic media, the rate determining step for the electrode process is the dismutation of the protonated hydrazo intermediate stabilized by the electron-attracting effect of the nitro group. Since this is a slow process, it produces two DPP peaks (whereas in DCP it yields two badly overlapping waves), one caused by the reduction from azo- to hydrazo-, the other one by the reduction of the quinoneimine (formed in the before mentioned dismutation) to amine. The anomalous E_p values observed for the second peak in the pH range 6–9, can be assigned to adsorption effects.

With increasing temperature a shift in the anodic sense is observed for both peaks (larger for the more cathodic one) as expected for a peak limited by the slow rate of a prior dismutation process.

In the pH range 9–13 only one peak is observed. Its height is approximately equal to the sum of the heights of the two peaks appearing in acidic media. This shows that the electroreduction must now be interpreted as a one-step process, directly to the amine stage, because the stabilizing effect of the nitro group on the intermediate ceases to be operative in this pH range. In ammonia–ammonium ion buffer solutions, a lesser adsorption or an increase in the electron-transfer rate is observed. It seems reasonable to accept that adsorption is modified as a consequence of a change in the orientation of the adsorbed molecules on the electrode surface due to the electrostatic repulsion forces exerted on the phenoxide groups. In the new orientation, the nitro group would remain in direct contact with the electrode surface, the naphthalene rings would be perpendicular to it, and the electroreducible azo group would stay far away from the surface. This orientation would allow an increase in the azocompound concentration at the electrode surface and would facilitate the reduction of the adsorbed molecules. The first peak is kinetic in character and corresponds to the discharge of the molecules adsorbed with the favoured orientation; the second or normal peak, appearing at more cathodic potential, corresponds to the discharge

of non-adsorbed reactant molecules or molecules adsorbed with a less favourable orientation[17,19]. This interpretation is coherent with the observed behaviour of the polarographic peaks in the presence of metal ions[20], since even in the presence of large excesses of these the height of the first peak remains constant, that of the second one strongly decreases, and peak potentials for both peaks do not show any variation with metal-ion concentration.

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