

Mechanism of 1-phenylazo-2-naphthol-3,6-disulphonic acid reduction on a mercury electrode

F CAPITAN*, A GUIRAUM, J L VILCHEZ and J M BOSQUE

Department of Analytical Chemistry, Analytical Section of CSIC, Faculty of Sciences, University of Granada, Granada, Spain

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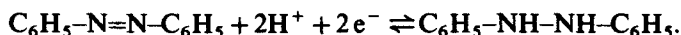
Abstract. The reduction of 1-phenylazo-2-naphthol-3,6-disulphonic acid (disodium salt) at the dropping mercury electrode has been investigated. The reduction takes place in a two-electron step. The process is diffusion controlled. The reagent captures two electrons and one or two hydrogen ions depending on whether the pH is higher or lower than 7, producing 1-phenylhydrazo-2-naphthol-3,6-disulphonic acid, in both cases. A disproportionation reaction of the hydrazo compound takes place, and amines are the final reduction products. The reaction orders, together with Tafel's slopes have been calculated.

Keywords. 1-Phenylazo-2-naphthol-3,6-disulphonic acid (disodium salt); polarography; cyclic voltammetry; azo dyes.

1. Introduction

There are a great number of papers in chemical literature related to the polarographic behaviour of azo compounds. They study either the electrode process itself or its analytical application. We have found that the compound referred to here can be applied to the polarographic determination of Ba(II). In order to elucidate the electrochemical behaviour of this reagent and its application to the determination stated above we have been surveying a good deal of the chemical literature related with polarography on azo compound.

The polarographic reduction of azobenzene was studied a long time ago (Shikata and Tachi 1931). The following equation was assigned to the reduction:



Subsequent studies showed a great diversity of opinion about the comprehension of the mechanism and its reversibility, due, mainly, to the experimental conditions (Wawzonek and Frederickson 1955). The studies by Nygard (1962, 1966) and Florence and collaborators (Florence 1965, 1974; Florence and Aylaward 1962; Florence and Farrar 1964; Florence *et al* 1974) contributed, decisively, to the explanation of the azo linkage reduction mechanism. Nygard (1966) studied the influence of the experimental conditions on the azobenzene reduction, using different polarographic methods. The half-wave potential dependence on the concentration is due, according to Nygard (1962), to the adsorption process. The hypothesis was confirmed (Holleck and Holleck 1964) (Wospeschall and Shain 1967). Nygard's suggestions were also supported by the

* To whom all correspondence should be addressed.

experimental work of Florence and Farrar (1964). Polarographic and controlled-potential coulometric studies of Eriochrome Violet-B have been done by Florence and Aylaward (1962). The electrode reaction involves four electrons, and amines are the final reduction products. This fact was explained by the formation of an unstable hydrazo intermediate which disproportionated, a hypothesis postulated earlier (Laitinen and Kneip 1956). Later, this hypothesis has been extensively verified by others (Florence 1965, 1974). The effect of substituents on the reduction of azo compounds has been studied (Florence 1965; Catchpole and Knaust 1960; Iijima and Sekido 1960; Iijima 1967). Groups such as hydroxy can cause the electrode reaction to involve more than two electrons.

We contribute to the knowledge of the subject, summarizing the results obtained on 1-phenylazo-2-naphthol-3,6-disulphonic acid reduction and finding good agreement with Florence *et al.*

2. Experimental

1-Phenylazo-2-naphthol-3,6-disulphonic acid (disodium salt) was synthesized by conventional diazotization with sodium nitrite in hydrochloric acid, followed by alkaline coupling (Giral and Rojahn 1956). Recrystallization was carried out from ethanol-water mixtures. The reagent was identified by elemental analysis and IR.

The *i*-*E* curves were recorded either automatically or traced point by point using a 471 AMEL multipurpose unit with the damping circuit completely suppressed. The potentials were measured *vs* SCE with a Crisom DIGIT 501 potentiometer, which was also used as a pH-meter. The cyclic voltammetry curves were recorded on a TECTRONIC SSP3 polarograph. The polarographic measurements were done using a thermostatted AMEL 494 cell. In all cases the temperature was maintained at $25.0 \pm 0.1^\circ\text{C}$. A saturated calomel reference electrode was used. The working electrode was a dropping mercury electrode (DME) with the following characteristics: rate of mercury flow 2.2 mg/sec, drop time 4.75 sec, open circuit, in a buffered solution at pH = 3.12 and the height of the mercury column was 41 cm. Britton-Robinson buffers were used as supporting electrolyte solutions (ionic strength 0.1 M). The working electrode for the cyclic voltammetry was an E410 Metrohm mercury hanging drop electrode. Controlled potential studies of a solution of 1-phenylazo-2-naphthol-3,6-disulphonic acid (disodium salt) in Britton-Robinson buffers pH 3.12 and 8.51 were carried out at a large stirred mercury pool electrode. The oxygen was removed by bubbling nitrogen gas (99.998% of purity) through the solution.

3. Results and discussion

3.1 Polarography

The 1-phenylazo-2-naphthol-3,6-disulphonic acid (disodium salt) reduced at the dropping mercury electrode produces one polarographic wave at different concentrations, temperatures and pH values. Figure 1 shows a representative polarogram at pH = 3.12. The nature of such a wave was investigated through the dependence of the limiting current on the height of the mercury and on the temperature. Thus the diffusive nature of the wave was demonstrated (Zuman 1969).

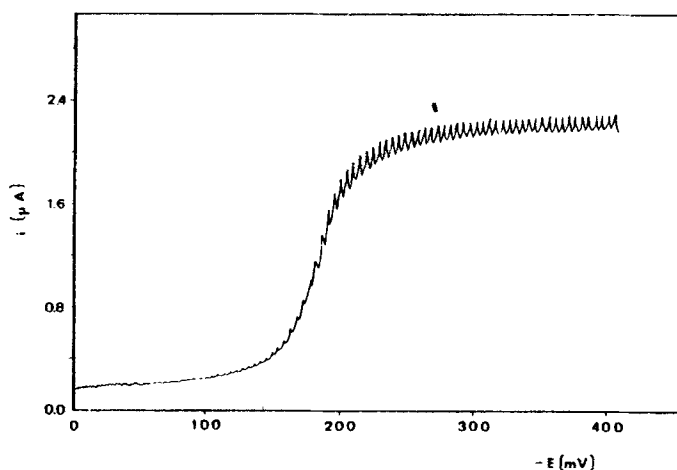


Figure 1. Polarogram of 2×10^{-4} M 1-phenylazo-2-naphthol-3,6-disulphonic acid (disodium salt) at pH 3.12.

We checked whether the limiting currents were proportional to the concentration of the reagent in the range between 8×10^{-5} and 4×10^{-4} M at pH 3.12 and 8.51. Linear segment slope values were $10.14 \text{ A} \times 1 \times \text{mmol}^{-1}$ and $1.05 \text{ A} \times 1 \times \text{mmol}^{-1}$ for pH 3.12 and 8.51, respectively. The half-wave potential shifts towards more negative values with an increase in concentration of the reagent. The diffusion current constant (I) was calculated from the Ilkovic equation, $I = 4.63$, and the diffusion coefficient $D = 1.45 \times 10^{-5} \text{ cm}^2 \times \text{sec}^{-1}$ at pH 3.12. Such values for I and D agree with previously published values of some azo compounds (Florence 1965, 1974; Florence and Aylward 1962; Florence *et al* 1974). The transfer coefficient determined from Tafel's slope (figure 2) is 0.58 and the order of reaction with respect to the concentration is

$$a = \left(\frac{\delta \log i}{\delta \log C} \right) E = 1.$$

The dependence of the half-wave potential on pH (table 1) was also studied in order to determine the number of hydrogen ions involved in the reduction. The log-plots of $E_{1/2}$ versus pH, showed two straight lines, the slopes of which were -100 and -50 mV. Hence, the number of hydrogen ions (p) involved in the reduction must be $p = 2$ and $p = 1$, respectively.

3.2 Coulometry

We carried out controlled-potential coulometry to determine n , *i.e.*, the number of electrons involved in the reduction. A mercury pool was used as the cathode and a platinum wire as the auxiliary electrode, the reference electrode was a saturated calomel electrode. The concentration of the sample before and after the electrolysis was measured polarographically to ensure that reduction reached completion. The samples contained 1.5×10^{-5} mol in 50 ml of solution. It appears that the reduction of 1-phenylazo-2-naphthol-3,6-disulphonic acid (disodium salt) involves 4.0 ± 0.1 electrons.

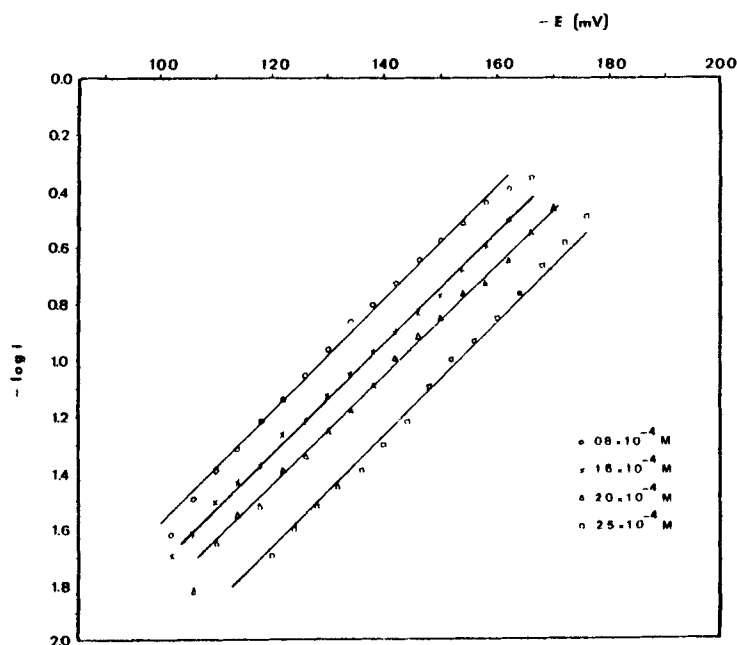


Figure 2. Representation of Tafel's equation for various reagent concentrations.

Table 1. Polarographic data 1-phenylazo-2-naphthol-3,6-disulphonic acid (disodium salt) 2×10^{-4} M.

pH	$E_{1/2}$ (mV)	$E_{3/4} - E_{1/4}$ (mV)	$n\alpha$
2.64	-140	-29	1.94
3.13	-194	-28	1.92
3.68	-240	-30	2.02
4.00	-281	-30	2.01
5.52	-429	-29	1.97
6.03	-482	-28	1.93
7.03	-572	-27	1.97
7.99	-632	-28	1.92
8.96	-672	-27	1.95
9.45	-692	-28	1.91

3.3 Cyclic voltammetry

The cyclic electrode voltammetric curves were recorded at different scan rates (figure 3). They always show a single cathodic wave, the anodic peak being absent. The shape of the cyclic voltammetry curve is in agreement with the diagnostic criteria proposed for systems in which an irreversible chemical reaction follows a reversible charge transfer (EC mechanism, Wopschall and Shain 1967). On the other hand, the plot of the current function ($i_p/(V)^{1/2}$) vs the scan rate (table 2 and figure 4), is in agreement with an

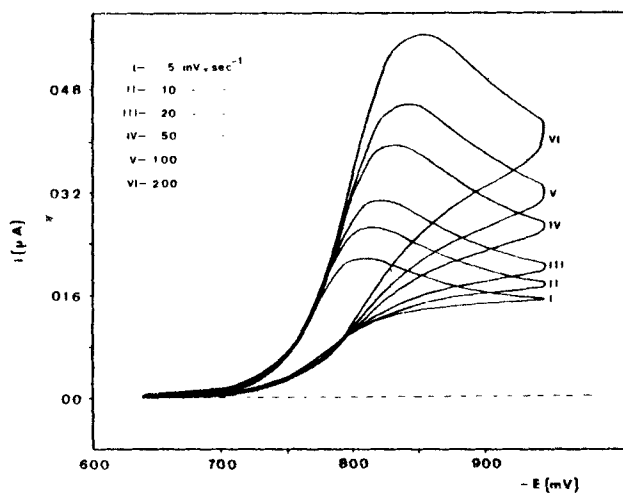


Figure 3. Cyclic voltammetric curves of 2×10^{-4} M 1-phenylazo-2-naphthol-3,6-disulphonic acid at pH 8.55.

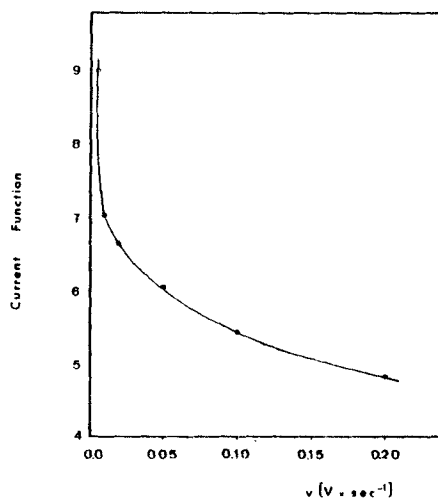


Figure 4. Variation of peak current functions ($i_p/(V)^{1/2}$) with rate of voltage scan.

Table 2. Cyclic voltammetric data of 1-phenylazo-2-naphthol-3,6-disulphonic acid (disodium salt) 2×10^{-4} M.

v (mV/sec)	i_p (μ A)	E_p (mV)	$E_{p/2}$ (mV)	$i_p/(V)^{1/2}$
5	0.64	-814	-764	9.01
10	0.74	-818	-768	7.04
20	0.94	-822	-770	6.66
50	1.36	-832	-780	6.07
100	1.72	-840	-788	5.44
200	2.20	-850	-796	4.92

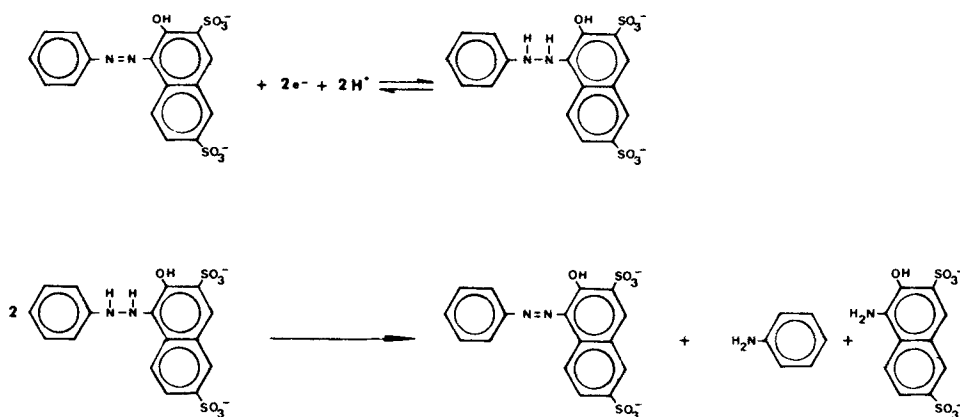


Figure 5.

irreversible catalytic reaction following a reversible charge transfer (Nicholson and Shain 1964).

4. Conclusions

The polarographic results obtained show that the reduction of 1-phenylazo-2-naphthol-3,6-disulphonic acid (disodium salt) proceeds by a diffusion controlled two-electron step. The reagent captures two electrons and two hydrogen ions at pH values lower than 7, whereas, at pH higher than 7 the reagent captures two electrons and one hydrogen ion, producing 1-phenylhydrazo-2-naphthol-3,6-disulphonic acid in both cases. The controlled potential coulometry report the consumption of four moles of electrons per mol of dye, confirming that there are four electrons involved in the reduction.

Cyclic voltammetry shows the existence of an irreversible catalytic reaction following the charge transfer step. These results are in agreement with previously obtained values for other azo compounds (Florence 1965) and we can accordingly attribute this reaction to the fast disproportionation of hydrazo compounds originating in the reduction. As a result we can say that one molecule of reagent as well as one molecule of each corresponding amine are regenerated (figure 5).

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