

## Reduction mechanism of 1,4-diamino-2,3-anthraquinone disulphonic acid

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**Abstract.** The potentiometric acid constants of 1,4-diamino-2,3-anthraquinonedisulphonic acid were calculated. The sequence of dissociation is discussed. The reduction of the reagent at a dropping mercury electrode has been investigated. The polarograms of reagent show two waves, whose adsorption and diffusion nature is respectively established. The reaction orders, together with Tafel's slopes have been calculated.

**Keywords.** Anthraquinones; polarography; potentiometry; reduction mechanism

### 1. Introduction

The diaminoanthraquinones are selective and sensitive reagents suitable for spectrophotometric and fluorimetric determination of a good number of metallic ions (Krausz *et al* 1963), but no attention seems to have been paid yet to their electrochemistry. 1,4-diamino-2,3-anthraquinonedisulphonic acid has been previously studied with respect to some analytical applications and has been proposed for the spectrophotometric determination of Au(III) (Capitán *et al* 1977), Pd(II) (Capitán *et al* 1982) and as an acid-base indicator (Capitán *et al* 1978).

In this paper the potentiometric dissociation constants are determined and the reduction of this reagent on a mercury electrode is studied.

### 2. Experimental

1,4-diamino-2,3-anthraquinonedisulphonic acid was synthesized according to Pattison's patent (Pattison *et al* 1957) by condensing 1,4-diamino-2,3-dichloroanthraquinone with boric acid and sulphuric acid to form a boric acid ester complex. The excess acid is neutralized and sodium sulfite added, replacing thus the chlorine atoms with sulphonic groups when heated at about 95°–100°C. The reagent was identified by elemental analysis, IR and NMR.

The acid-dissociation constants of reagent have been determined by the potentiometric Bjerrum's (1941) method at ionic strength  $\mu = 0.1$ , from the titrations of the free acid, monosodium salt and disodium salt performed with a Metrom-Herisau E-536 potentiograph.

The *i-E* curves were registered either automatically or traced point by point using a

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471 Amel multipurpose unit with the damping circuit completely suppressed. The cyclic voltammery curves were recorded on a Tektronix ssp 3 polarograph. The potentials were measured *vs.* SCE with a Radiometer PHM-84 potentiometer which was also used as a pH-meter.

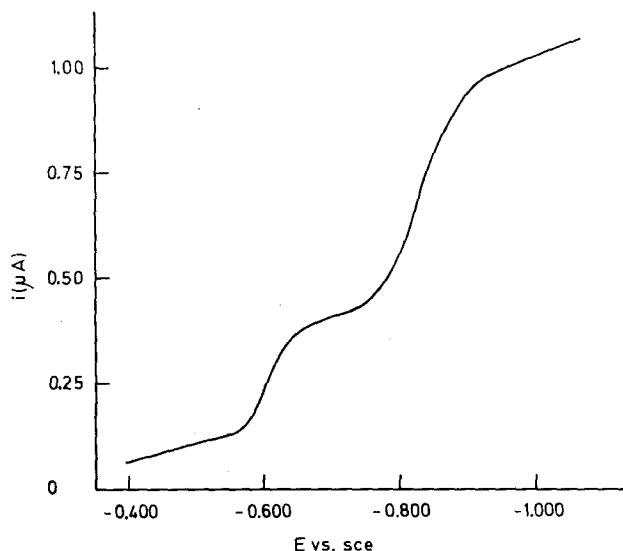
The polarographic measurements were made using a thermostated Amel 494 cell. A saturated calomel reference electrode was used. The working electrode was a mercury capillary with the following characteristics: rate of mercury flow  $m = 1.95$  mg/sec, drop time  $t = 5.15$  sec, open circuit, in a buffered solution at pH 12.15 and the height of the mercury column  $h = 42.50$  cm. The cyclic voltammery curves were found out using a hanging drop electrode as working electrode.

All the reagents used were Merck AR grade. As a supporting electrolyte solution, a buffered solution of  $6.66 \times 10^{-2}$  M  $\text{Na}_3\text{PO}_4$  and 0.1 M.  $\text{H}_3\text{PO}_4$  mixed in varying proportions according to the pH desired was used. The ionic strength was adjusted with  $\text{KNO}_3$  to 0.24 M. All the measurements were done in an atmosphere of nitrogen and at a temperature  $25.0 \pm 0.1$  °C.

### 3. Results

The acid-dissociation constants of 1,4-diamino-2,3-anthraquinonedisulphonic acid were determined potentiometrically (Bjerrum 1941) at ionic strength  $\mu = 0.1$ . A maximum of two dissociation constants have been determined in the range of pH investigated and their pK values are  $\text{pK}_1 = 3.91$  and  $\text{pK}_2 = 8.15$ .

The 1,4-diamino-2,3-anthraquinonedisulphonic acid reduced on the DME produce two polarographic waves from aqueous solutions at concentrations smaller than  $1.6 \times 10^{-3}$  M. Both waves were always observed throughout the complete pH range studied (2.00–12.71). Figure 1 shows a representative polarogram at pH 12.50 ( $E_1$ )<sub>1</sub> = -0.616 V, and ( $E_1$ )<sub>2</sub> = -0.848 V.



**Figure 1.** Polarogram of  $4 \cdot 10^{-4}$  M 1,4-diamino-2,3-anthraquinonedisulphonic acid at pH 12

The nature of such waves was investigated through the dependence of the limiting current on the height of the mercury column and the temperature. Thus the adsorptive and diffusive nature of the first and the second wave respectively were proved (Zuman 1969).

The dependence of the half-wave potential on pH was studied as well, to determine how many hydrogen ions are involved in the reduction. Polarograms were recorded for  $2 \times 10^{-4}$  M solutions in the pH range 5.60–12.72.  $E_{1/2}$  and  $n\alpha$  values were calculated in each case. Figure 2 shows the plots of  $E_{1/2}$  vs pH. One can observe two straight lines the slopes of which are 62 mV and 28 mV depending on whether pH is lower or higher than 8.27. Accordingly, the number of hydrogen ions involved in the reduction must be either  $p = 2$  or  $p = 1$  respectively.

On the other hand, we checked whether the limiting currents are proportional to the concentration of the 1,4-diamino-2,3-anthraquinonedisulphonic acid in the bulk of the solution, in the range  $5 \times 10^{-3}$  M– $4 \times 10^{-5}$  M at pH 12.50. The values of the slope of the linear segments are:  $1.65 \mu\text{AL}/\text{mM}$  and  $3.10 \mu\text{AL}/\text{mM}$  for the first and the second wave respectively. Hence, the diffusion current constants are  $I = i_d/m^{2/3} t^{1/6}$ ,  $C = 607 D^{1/2} n = 1.51$  calculated for the second wave, and the diffusion coefficient is  $D = 1.55 \times 10^{-6} \text{ cm}^2/\text{sec}$ . Such  $I$  and  $D$  values agree with those previously published for some anthraquinone (Capitán *et al* 1979, 1980, 1981).

The half-wave potentials  $E_{1/2}$  remains independent with an increase in concentration.

The transfer coefficient determined from Tafel's slope is  $\alpha = 0.48$  and the order of reaction with respect to the concentration is:

$$\left| \frac{d \log i}{d \log C} \right|_E = 1$$

calculated from the second wave.

We carried out controlled potential microcoulometry to determine  $n$ , i.e., the number of electrons involved in the reduction. It appears that the reduction of

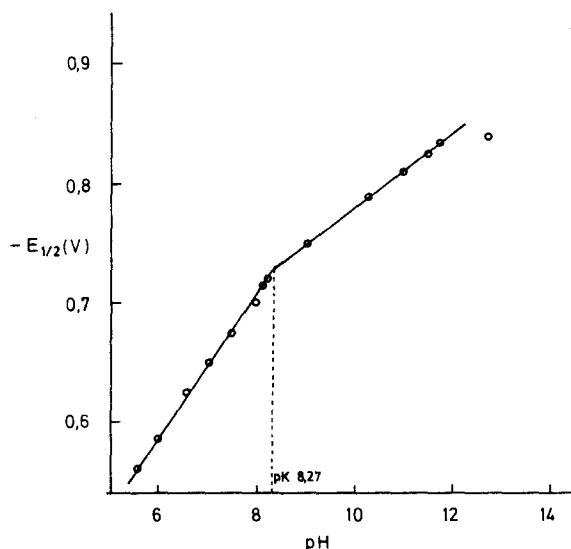


Figure 2. Dependence of half-wave potential on pH for the second wave.

1,4-diamino-2,3-anthraquinonedisulphonic acid involves two electrons.

The cyclic voltammetric curves for both waves at different scan rates and concentration were registered showing always two cathodic peaks and one anodic peak respectively. The main observed features are:

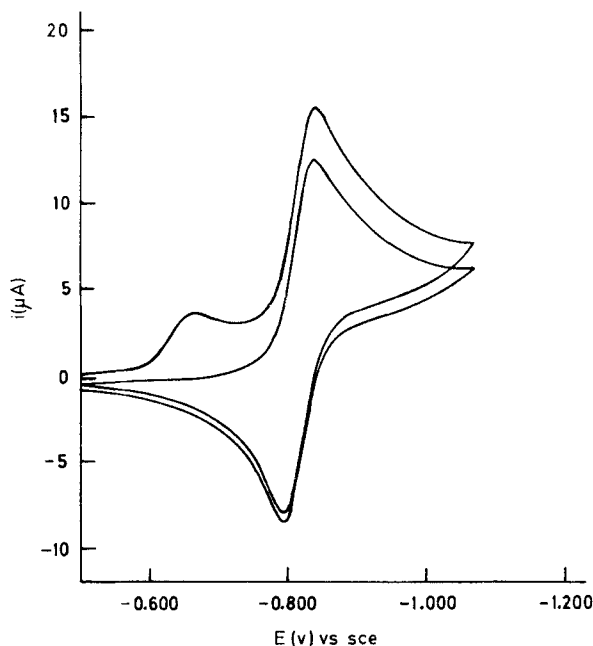
(a) Successive voltammograms obtained at different sweep rates show that the first wave disappears when a second cycle is imposed immediately after the first and the sweep rate is higher than 20 mV/sec (figure 3). This confirms the adsorption nature of the first wave. Such behaviour has been observed by Ali-Qureshi *et al* (1979) for a similar reagent.

(b) The cathodic (positive) and anodic (negative) peak currents for the second wave are virtually identical; the peak separation  $E_{P(c)} - E_{P(a)}$  being 33 mV, which is not far from the theoretical value of 30 mV for a bielectronic transference. Hence, one can say that the reduction of reagent is reversible under such conditions. On the other hand the plots of  $i_p$  vs.  $\log v$  at different concentrations are linear with slopes of 0.5, in agreement with theoretical value.

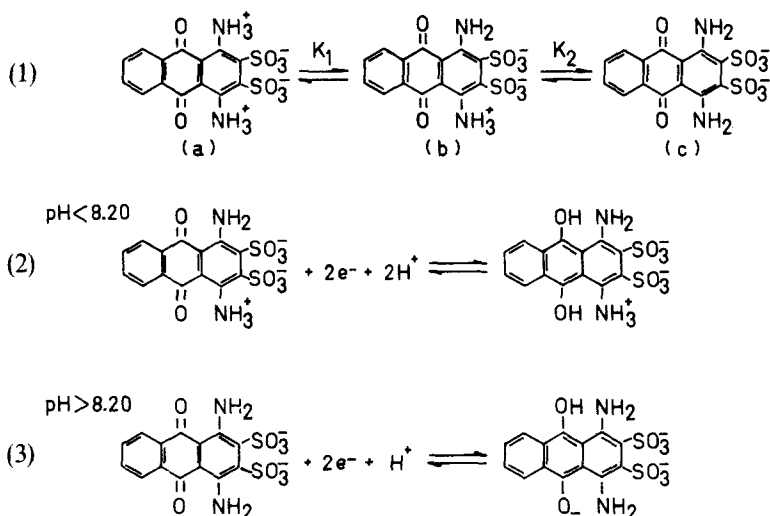
(c) The  $\alpha$  and reactions order values calculated from this technique agree with those previously calculated polarographically.

#### 4. Discussion

The acid dissociation constant values obtained potentiometrically as well as the strong acidic nature of the sulphonic groups (being thus extensively dissociated) suggest that in



**Figure 3.** Successive cyclic voltammetry curves of  $4 \cdot 10^{-4}$  M 1,4-diamino-2,3-anthraquinonedisulphonic acid at pH 12.



aqueous solution the 1,4-diamino-2,3-anthraquinonedisulphonic acid is structured mainly as in scheme 1a. Owing to its structure, (a) is a rather strong acid ( $\text{p}K_1 = 3.91$ ) and it may be easily dissociated to give the structure as in scheme 1b. Finally it can dissociate ( $\text{p}K_2 = 8.15$ ) to give a structure as in scheme 1c.

These dissociation steps agree with those found for similar molecules (García-Sánchez *et al* 1970).

Moreover, here, the polarographic curves show that the reduction of the 1,4-diamino-2,3-anthraquinonedisulphonic acid proceeds by one bielectronic step diffusion controlled in basic medium, showing specific adsorption of the reagent at the mercury electrode. The reagent requires two electrons and two protons at pH lower than 8.20 and two electrons and one proton at pH higher than 8.20, to produce the respective hydroquinone. The shape of the cyclic voltammetry curves is, in agreement with the diagnostic criteria proposed for a EE mechanism at the investigated scan rates.

From the results and conclusions obtained and in accordance with the dissociation steps of the reagent, we propose for the reduction of 1,4-diamino-2,3-anthraquinonedisulphonic acid, a mechanism with the following reaction pathways: (a) At pH lower than 8.20 the predominant form is as in scheme 1b, which captures two electrons and two protons to form a hydroquinone system. (scheme 2). (b) At pH higher than 8.20 the predominant form is as in scheme 1c, which captures two electrons and one proton to form a hydroquinone system (scheme 3).

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