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# Electrochemical reduction of 2-ethyl-9,10-anthraquinone on reticulated vitreous carbon and mediated formation of hydrogen peroxide

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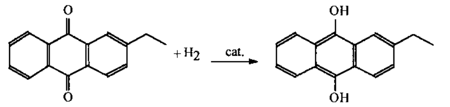
Hydrogen peroxide formation by the intermediate electroreduction of 2-ethylanthraquinone (EAQ) has been examined. The medium used for this preparative electrolysis was dimethoxyethane (DME) with tetraethylammonium tetrafluoroborate (TEATFB) salt as supporting electrolyte in the presence of a small percentage of water. In this process EAQ is reduced on a reticulated vitreous carbon (RVC) cathode in the presence of oxygen. It has been demonstrated that in this medium, the presence of EAQ enhances the hydrogen peroxide formation when compared to the direct reduction of oxygen in the same medium. The influence of EAQ on the oxygen reduction has also been examined by cyclic voltammetry on a vitreous carbon cathode.

Keywords: *cyclic voltammetry*, *reduction*, *oxygen*, *2-ethyl-9,10-anthraquinone*, *hydrogen peroxide*, *reticulated vitreous carbon (RVC)*

## 1. Introduction

2-ethyl-9,10-anthraquinone (EAQ) is used in the anthraquinone process for the large-scale manufacture of hydrogen peroxide (AO process) [1]. After the dissolution of anthraquinone in a suitable mixture of solvents, this working solution reacts with hydrogen in the presence of a catalyst to form the corresponding hydroquinone. After the catalyst is removed from the solution, the hydroquinone is oxidized to quinone with oxygen, with simultaneous formation of hydrogen peroxide, corresponding to Reactions 1 and 2.



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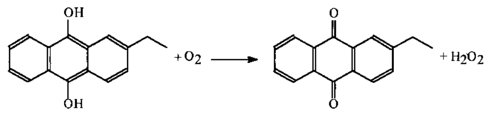

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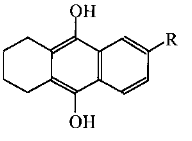
Hydrogen peroxide is extracted with water and the quinone is recycled.

The catalytic hydrogenation has low selectivity and leads to undesired products such as 2-alkyl-5,6,7,8-tetrahydro-9,10-dihydroxy-anthracene (**I**) which is the result of hydrogenation of the unsubstituted ring of the quinone. Another undesired product is oxanthrone (**II**) which is produced following the hydrogenation of only one carbonyl group. Anthrone (**III**) and dimer (**IV**) can be formed as derivatives from this product. In the oxidation step, the compound (**I**) can lead to an epoxide byproduct, (**V**). Moreover, the catalyst must be completely removed from the solution before the oxidation step, to prevent decomposition of the hydrogen peroxide.



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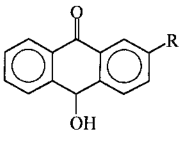

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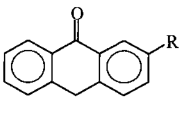

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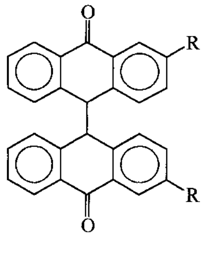

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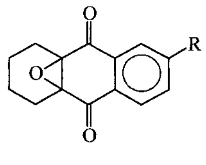

(V)

To avoid the above mentioned difficulties, some authors have studied different approaches for the hydrogenation step. Thus Lynn and Paalman proposed a process for hydrogen peroxide production based on an intermediate, the disodium salt of 2-ethyl-anthrahydroquinone ($EAQNa_2$) [2, 3]. In this process, the reducing agent was a sodium amalgam. Calabrese and Wrighton investigated the photoelectrochemical reduction of 2-*t*-butyl-9,10-anthraquinone as an approach to the synthesis of hydrogen peroxide [4]. Keita and Nadjo also studied the hydrogenation step by an electrochemical route [5]. The quinone used was 9,10-anthraquinone-2,6-disulfonic acid soluble in aqueous solutions. Knarr *et al.* studied

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the electrochemical reduction of 2-ethyl-9,10-anthraquinone [6]. They also produced the disodium salt $EAQNa_2$ in a two-phase system in the absence of oxygen. Under well-defined conditions, they obtained current efficiencies approaching 100% with current densities of $15\,mA\,cm^{-2}$. The goal of these different studies is to avoid the low selectivity of the catalytic hydrogenation, and the necessity to remove the catalyst before the oxidation step.

With the same objective we have studied hydrogen peroxide production mediated by electrochemically reduced EAQ in an organic medium in the presence of water. In this paper we describe a cyclic voltammetric study of EAQ in 1,2-dimethoxyethane (DME) on a vitreous carbon electrode in the presence of water. The tetraethylammonium tetrafluoroborate (TEATFB) is used as supporting electrolyte. In the same conditions we also examine the preparation of hydrogen peroxide by the intermediate electroreduction of EAQ on reticulated vitreous carbon (RVC).

## 2. Experimental details

### 2.1. *Products*

1,2-dimethoxyethane (DME) (Fluka), 2-ethyl-9,10-anthraquinone (EAQ) (Aldrich) were used without further purification. The supporting electrolyte was tetraethylammonium tetrafluoroborate (TEATFB) (Fluka).

### 2.2. *Apparatus*

Voltammetric measurements were performed with a scanning potentiostat (model 362 EG&G, Princeton Applied Research). Voltammetric curves were plotted on a X–Y plotter (model SE 780, Asea Brown Bovery). The cell was from Metrohm and the two compartments were separated by a Nafion® 117 membrane. The working electrode was a vitreous carbon ($7\,mm^2$) disc and the counter electrode was made of platinum. The reference was a Hg/HgO/NaOH 1 M ($E^\circ = 0.098\,V$ vs NHE) electrode. All measured potentials are related to this reference. The 'apparent pH' was determined using a combined glass electrode (Metrohm). The oxygen or nitrogen flow rate was $50\,ml\,min^{-1}$.

Electrosynthesis was conducted in the same Metrohm cell. The cathodes used were blocks of reticulated vitreous carbon (RVC) of different grades. The anode was platinum. A scheme of the electrosynthesis cell is given in Fig. 1.

### 2.3. *Procedure*

The investigation on the EAQ behaviour was performed in oxygen-free solution by bubbling nitrogen through it for one hour and during the course of the experiment a blanket of nitrogen was maintained over the solution. A reference voltammogram was recorded before the EAQ was added to the mixture of solvent-electrolyte.

For the investigations in the presence of oxygen the mixture was previously saturated with oxygen with a $50\,ml\,min^{-1}$ flow. A reference voltammogram of the oxygen saturated mixture without EAQ was recorded. All measurements were made at room temperature.

The electrosyntheses were conducted at controlled current in the presence of oxygen in the same cell. The hydrogen peroxide formation was followed by spectrophotometric determination of a Ti(IV)–$H_2O_2$ complex [7].

## 3. Results and discussion

### 3.1. *Voltammetric studies*

The choice of the medium in which these voltammetric studies were performed was guided by pre-

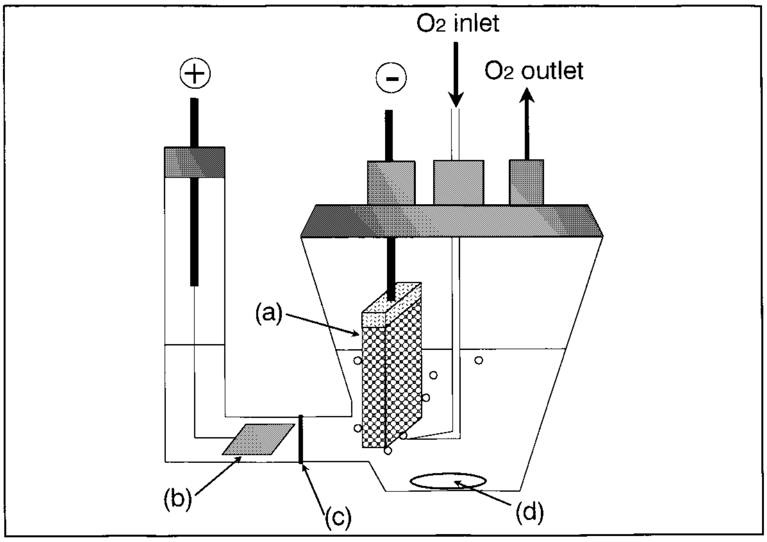

Fig. 1. Scheme of the Metrohm cell (upper diam. 8 cm, max. vol. 100 ml): (a) RVC electrode; (b) platinum sheet; (c) Nafion® 117 membrane; (d) magnetic stirrer.

liminary experiments on preparative electrolysis of hydrogen peroxide. It turned out that DME and tetrabutylammonium hydroxide (TBAH) in the presence of water, as used in our first investigations in this domain [8], did not provide satisfying conditions for use in preparative electrolysis. This was due to a too low conductivity through the membrane. The use of a tetraethylammonium salt immediately provided good conditions for the preparative electrolysis of hydrogen peroxide. Thus the voltammetric studies were performed in DME + $10^{-1}$ M TEATFB + 5% $H_2O$.

*3.1.1. Electrochemical behaviour of EAQ in the absence of oxygen.* Figure 2(a) shows a cyclic voltammogram at 200 mV $s^{-1}$ of 2 $\times 10^{-3}$ M EAQ in the medium described above. Water provided good conditions for the dissolution of TEATFB and a weak proton source. In this medium (pH 10.6), EAQ is reduced in two steps corresponding to the following reactions:

$$EAQ + e^- \leftrightarrow EAQ^{\bar{\bullet}} \qquad (3)$$

$$EAQ^{\bar{\bullet}} + e^- + H_2O \leftrightarrow EAQH^- + OH^- \qquad (4)$$

It has been established that, in these pH conditions, the proton is involved in the second reduction step and the dianion $EAQ^{-}$ cannot be obtained [8].

The apparent pH of the medium is 10.6. If we compare this with our preliminary investigations of the behaviour of EAQ ($C = 2 \times 10^{-3}$ M) in DME + $10^{-1}$ M TBAH + different quantities of 0.2 M $HClO_4$ [8], results of the present study agree with those observed earlier. The EAQ behaviour observed in DME + $10^{-1}$ M TEATFB + 5% $H_2O$ at pH 10.6 corresponds to those observed at a higher pH (~13) in DME + $10^{-1}$M TBAH + 17.5 ml 0.2 M $HClO_4$; this mixture contained about 30% of water. At lower pH the EAQ is reduced in one step involving two electrons and two protons. The difference value for the pH is due to the different components in the medium which affect the apparent pH used in our comparative scale.

*3.1.2. Electrochemical behaviour of oxygen in the absence of EAQ.* Figure 2(b) shows the voltammogram obtained under the same conditions as before with a pure oxygen saturated solution in the absence of EAQ.

The oxygen reduction occurs in two steps involving two electrons:

$$O_2 + 2e^- + H_2O \leftrightarrow HO_2^- + OH^- \qquad (5)$$

$$HO_2^- + 2e^- + H_2O \leftrightarrow 3OH^- \qquad (6)$$

the high currents observed are due to the good solubility of oxygen in this medium.

*3.1.3. Electrochemical behaviour of oxygen in the presence and in the absence of EAQ.* Figure 3 shows the voltammograms obtained in the same conditions as before in the absence (a) and presence (b) of EAQ. When we compare the curves (a) and (b) the oxygen reduction peak potentials are shifted toward less negative values compared with those obtained without EAQ. The shifts are 100 and 80 mV for the first and second wave, respectively. The lowering in reduction peak current can be attributed to the coating of the vitreous carbon surface by organic species. The shift of the cathodic peak potentials has been observed by several authors working on the reduction of oxygen with quinone containing polymer coated electrodes [9–11]. This phenomenon can be explained by the following reactions:

$$EAQ + e^- \leftrightarrow EAQ^{\bar{\bullet}} \qquad (3)$$

$$EAQ^{\bar{\bullet}} + e^- + H_2O \leftrightarrow EAQH^- + OH^- \qquad (4)$$

$$EAQH^- + O_2 \leftrightarrow EAQ + HO_2^- \qquad (7)$$

$$EAQ + e^- \leftrightarrow EAQ^{\bar{\bullet}} \qquad (3)$$

Reaction 7 is linked to the reduction peak of oxygen which is strongly shifted positively when compared to the peak observed in the absence of the quinone.

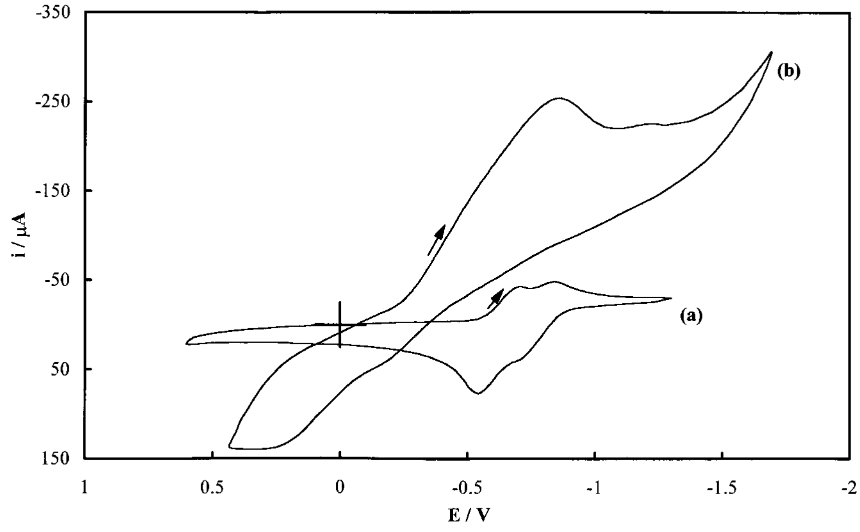

Fig. 2. Cyclic voltammograms ($v = 200$ mV $s^{-1}$) of (a) DME + $10^{-1}$ M TEATFB + 5% $H_2O$ + 2 × $10^{-3}$ M EAQ, without $O_2$; (b) DME + $10^{-1}$ M TEATFB + 5% $H_2O$, $O_2$ saturated.

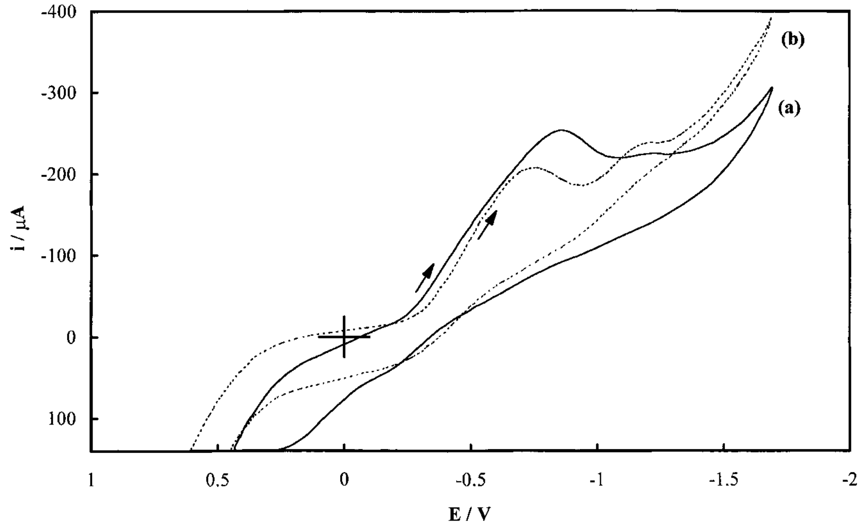

Fig. 3. Cyclic voltammograms ($v = 200\,\mathrm{mV\,s^{-1}}$) of (a) DME + $10^{-1}$ M TEATFB + 5% $H_2O$, $O_2$ saturated, (b) same as (a) + $2 \times 10^{-3}$ M EAQ, $O_2$ saturated.

### 3.2. *Preparative electrolysis of hydrogen peroxide by the intermediate reduction of EAQ*

These electrolyses were carried out in the medium DME + $10^{-1}$ M TEATFB + 5% $H_2O$ on RVC in the presence of oxygen.

*3.2.1. Comparison with the preparation of hydrogen peroxide by direct reduction of oxygen.* In this experiment the RVC was 60 ppi grade ($a_e = 35\,\mathrm{cm^{-1}}$) with dimensions 2.4 cm × 0.5 cm × 2.0 cm (total area of 84 $\mathrm{cm^2}$). The electrolysis current was 42 mA, which gives a current density of 0.5 $\mathrm{mA\,cm^{-2}}$. The oxygen reduction reaction is

$$O_2 + 2e^- + H_2O \leftrightarrow HO_2^- + OH^- \qquad (5)$$

The result of this electrolysis is shown in Fig. 4. The low current efficiency is due to the loss of hydrogen peroxide by the competitive reaction:

$$HO_2^- + 2e^- + H_2O \leftrightarrow 3OH^- \qquad (6)$$

In the presence of EAQ the results shown in Fig. 4 are clearly better. In this case, the decrease in current efficiency is also attributed to Reaction 6. But the current efficiencies were distinctly higher than those obtained without EAQ under the same conditions.

It can be concluded that the reduction of $O_2$ by the reduced form of EAQ can take place in such a medium. This phenomenon can be explained by the following reactions:

$$EAQ + 2e^- + H_2O \leftrightarrow EAQH^- + OH^- \qquad (8)$$

$$EAQH^- + O_2 \leftrightarrow EAQ + HO_2^- \qquad (7)$$

Equation 7 assumes a chemical homogeneous reaction between the reduced species $EAQH^-$ and the dissolved oxygen within the medium. However, we cannot exclude a reaction in the neighbourhood of the electrode corresponding to:

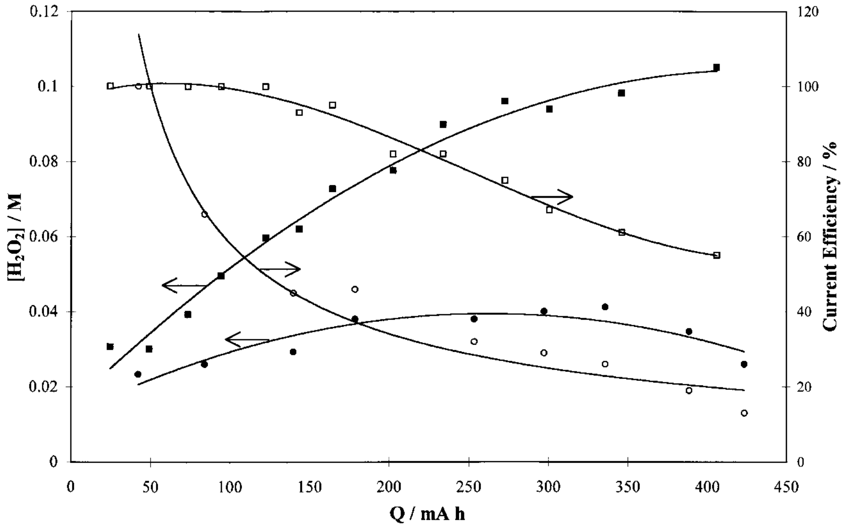

Fig. 4. Comparison of hydrogen peroxide formation in DME + $10^{-1}$M TEATFB + 5% $H_2O$: by direct reduction of $O_2$ (50 ml $\mathrm{min^{-1}}$) in the absence of EAQ, (●) [$H_2O_2$] (M) and (○) current efficiency (%); by indirect reduction of EAQ ($2 \times 10^{-3}$ M) in the presence of $O_2$ (50 ml $\mathrm{min^{-1}}$), (■) [$H_2O_2$] (M) and (□) current efficiency (%).

$$\mathrm{EAQH^- + O_2 + e^- \leftrightarrow EAQ^{\bar{\bullet}} + HO_2^-} \qquad (9)$$

*3.2.2. Results of the electrolyses.* Different experiments were carried out on RVC of the following grades: 45 ($a_e = 28\,\mathrm{cm^{-1}}$), 60 ($a_e = 35\,\mathrm{cm^{-1}}$) and 80 ($a_e = 50\,\mathrm{cm^{-1}}$) pores per inch. Due to differences in electrode dimensions, the total areas of the electrodes were: 67, 84 and 72 cm$^2$, respectively. The effect of current density was examined between 0.5 and 0.8 mA cm$^{-2}$. In all cases, results close to those of Fig. 4 were obtained; that is steady state concentrations of about 0.1 M with current efficiencies slightly over 50%. But for current densities higher than 0.9 mA cm$^{-2}$ the current efficiencies decreased drastically. This is due to the reduction of hydrogen peroxide by Reaction 6. With the concentration of hydrogen peroxide increasing, the potential of the electrode changes and promotes reduction (6). Hydrogen evolution was also observed at these current densities.

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