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Electrochemical reduction of 2-ethyl-9,10-anthraquinone (EAQ) and mediated formation of hydrogen peroxide in a two-phase medium

Part I: Electrochemical behaviour of EAQ on a vitreous carbon rotating disc electrode (RDE) in the two-phase medium

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The electrochemical reduction of 2-ethyl-9,10-anthraquinone (EAQ) has been examined by voltammetry on a vitreous carbon rotating disk electrode (RDE) in a two-phase medium. The medium consisted of an organic phase consisting of a mixture of tributylphosphate (TBP) and diethylbenzene (DEB) (15/85, vol/vol) and an aqueous phase, 2 M NaOH. The ratio between the two phases was 40% for the organic phase and 60% for the aqueous phase. The electrochemical behaviour of EAQ in this medium was examined on a vitreous carbon RDE in the presence and absence of oxygen. The formation of hydrogen peroxide mediated by the electrochemical reduction of EAQ was studied analytically. The voltammetric results indicate that hydrogen peroxide formation mediated by the electrochemical reduction of EAQ is feasible.

Keywords: *2-ethyl-9,10-anthraquinone*, *oxygen*, *electroreduction*, *voltammetry*, *two-phase*, *vitreous carbon*

1. Introduction

For many organic electrochemical processes it is difficult to achieve high mass transfer rates due to the low solubility of reacting species in the aqueous phase. The use of a two-phase medium is one approach to enhance the mass transfer conditions; the organic phase acts as a reservoir for the reacting species and a promoter of turbulence.

Different process techniques are distinguished for two-phase electrolysis [1]:

(a) Electrolysis of an organic phase containing the substrate in emulsion with an aqueous phase. Here the two-phase mixed electrolytes serves to saturate the aqueous phase with the substrate which is converted at the aqueous/electrode interface.

(b) Addition of a mediator system to the aqueous phase which is continuously regenerated at the electrode. Again, the two-phase medium serves to saturate the aqueous phase with the substrate where it is chemically converted by the mediator.

(c) Addition of a phase-transfer catalyst to transfer the mediator in the organic phase, which is soluble in the aqueous phase and regenerated at the electrode. The substrate is chemically converted in the organic phase where it is most soluble.

(d) The use of two-phase mixed electrolytes where the substrate dissolved in the organic phase is electrochemically converted at the organic/electrode interface. The aqueous electrolyte is necessary to insure a high conductivity. It also serves as a reactant for the electrochemical reaction.

The investigations presented in this paper are related to case (d). The use of liquid–liquid emulsions enhances the mass transfer conditions, thus improving the process efficiency. To understand this improvement, some authors have studied mass transfer using different electrode configurations.

First Wendt and Dworak showed two mechanisms associated with mass transfer in a two-phase electrolyte: the boundary layer compression mechanism and the ‘wetting’ mechanism [2, 3]. Wendt and Feess examined these phenomena in a trickle cell [4]. Alkire and Lu studied mass transfer in a parallel plate electrolyser with two-phase liquid–liquid flow [5, 6] and introduced the notion that global mass transfer in parallel plate electrolysers with a two-phase flow is a combination of three effects: (i) the contribution of single-phase flow; (ii) the disturbance by the presence of the second phase; and (iii) the replenishment of reactant by extraction from the second phase.

Alkire and Fenton also studied the mass transfer in flow-through porous electrodes with two-phase liquid–liquid flow [7, 8]. They expressed the overall mass transfer rate as a combination of four effects: (i) the contribution of single phase flow as if it were flowing alone; (ii) the decrease in mass transfer due to an effect of electrode coverage by dispersed liquid droplets; (iii) the contribution of mass transfer between the two-phase; and (iv) the further enhancement due to the penetration of the mass-transfer boundary layer by dispersed droplets containing the reactant.

The electrochemical reduction of 2-ethyl-9,10-anthraquinone (EAQ) and the mediated formation of hydrogen peroxide in a two-phase medium are representative of phenomena mentioned above.

To study the behaviour of the EAQ in a two-phase medium in the presence and absence of oxygen, a system was developed that allowed a voltammetric study of the substrate dissolved in the organic phase. Good voltammetric curves were obtained using a rotating disc electrode (RDE) in the two-phase medium under strong agitation to maintain emulsion uniformity. The choice of the RDE material was vitreous carbon. The approach was similar to conditions used in electrolysis where a porous cathode made of reticulated vitreous carbon (RVC) has been used. The two-phase medium consists of a mixture of tributylphosphate (TBP) and diethylbenzene (DEB) (15/85, vol/vol) containing EAQ dispersed in 2 M NaOH. The voltammetric study was made in a mixture containing 40% of the organic phase and 60% of the aqueous phase. Under these conditions the aqueous phase is continuous. The voltammetric curves of EAQ reduction in the presence and absence of oxygen were compared.

2. Experimental details

2.1. *Products*

2-ethyl-9,10-anthraquinone (EAQ), tributylphosphate (TBP) and diethylbenzene (DEB) were obtained from Aldrich and were used without further purification. The 2 M NaOH aqueous solution was prepared with sodium hydroxide from Fluka and distilled water.

2.2. *Apparatus*

Voltammetric measurements were performed with a scanning potentiostat (model 362, EG&G Princeton Applied Research). Voltammetric curves at slow potential sweep rate ($2\,\mathrm{mV\,s^{-1}}$) were stored and processed using a data acquisition system (ATMIO 16F5 card and Labview software, National Instruments). The cell was from Metrohm and the two compartments were separated by a Nafion® 117 membrane. The rotating disc electrode (RDE) was a vitreous carbon ($7\,\mathrm{mm^2}$) disc and was adapted to fit the rotor of a Tacussel (model CTV101T) instrument. The counter electrode was made of platinum. The reference was a Hg/HgO/1 M NaOH ($E^\circ = 0.098$ V vs NHE) electrode. All measured potentials are given related to this reference. The O_2 and N_2 flow rates were $50\,\mathrm{ml\,min^{-1}}$ and were regulated using two flowmeters (Hi-Tech model 5500).

2.3. *Procedure*

Experiments were performed in an oxygen-free solution by bubbling nitrogen through it for 1 h. During the course of the experiments a blanket of nitrogen was maintained over the solution. For the investigations in the presence of oxygen the mixture was saturated with O_2. The same experiments were carried out in the two-phase medium without EAQ to compare oxygen reduction in the presence and absence of EAQ. For all voltammetric measurements, a constant agitation was maintained in the cathodic compartment to ensure a good emulsion of the dispersed phase in the 2 M NaOH.

3. Results and discussion

It was impossible to obtain voltammograms at rotation rates lower than 2000 rpm because the hydrodynamic conditions were not sufficient to allow renewal of the vitreous carbon surface. Vitreous carbon is hydrophobic and an organic droplet may adhere to the electrode surface. A minimum rotation rate of 2000 rpm was necessary to avoid this phenomenon.

3.1. *Investigation of the electrochemical behaviour of EAQ in the absence of oxygen*

A two-phase medium containing 22.5 ml of 2 M NaOH and 15 ml of the mixture of TBP and DEB was used. The EAQ concentration was 2×10^{-2} M in the organic phase. Figure 1(α) shows the voltammogram obtained for a rotation rate of 2000 rpm. The reduction reaction observed is attributed to the following equation:

$$\mathrm{EAQ} + 2\,\mathrm{e}^- + \mathrm{H_2O} \rightarrow \mathrm{EAQH}^- + \mathrm{OH}^- \qquad (1)$$

In this medium, one step was observed, the reaction suggests two electrons. We showed that EAQ reduction in another strong alkaline solution (dimethoxyethane (DME) with tetrabutylammonium hydroxide (TBAH) as supporting electrolyte) proceeds through two single electron transfer steps [9].

For an accurate determination of the half-wave potential for the reduction reaction, we used curves of $\mathrm{d}i/\mathrm{d}E$ against E calculated from the i against E curves. Using the $E_{1/2}$ values, the limiting current was measured from the i against E curves. Table 1 summarizes the $E_{1/2}$ and i_L obtained for different rotation rates for the EAQ reduction.

3.2. *Reduction of O_2 in the two-phase medium in the absence of EAQ*

Figure 1(β) shows the voltammogram obtained at 2000 rpm in the two-phase medium saturated with O_2

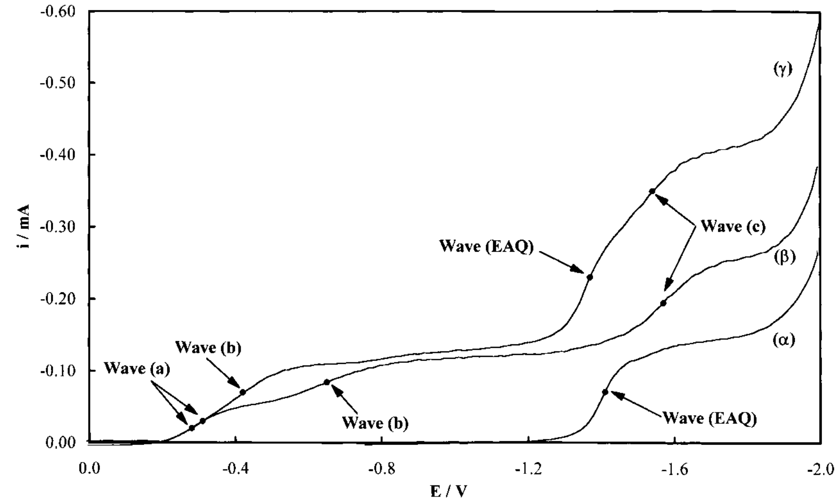

Fig. 1. Voltammograms at a vitreous carbon RDE in the two-phase medium TBP/DEB (15/85, vol/vol) + 2 M NaOH (40/60, vol/vol), rotation rate = 2000 rpm, potential scan rate = 2 mV s^{-1}. (α) containing 2×10^{-2} M EAQ in the organic phase, without oxygen; (β) without EAQ, in the presence of oxygen; (γ) containing 2×10^{-2} M EAQ in the organic phase, in the presence of oxygen. The symbol (•) indicates the half-wave potential determined by the di/dE against E curves.

Table 1. Half-wave potentials and limiting currents for the EAQ reduction in the absence of oxygen

Rotation rate/rpm	$E_{1/2}$/V	$i_L^{(EAQ)}$/mA
2000	−1.4	−0.14
3000	−1.4	−0.16
4000	−1.4	−0.18
5000	−1.39	−0.21

with the absence of EAQ. The following reactions are attributed to the observed plateaux:

Wave (a) $O_2 + e^- \rightarrow O_2^{-\cdot}$ (2)

Wave (b) $O_2^{-\cdot} + e^- + H_2O \rightarrow HO_2^- + OH^-$ (3)

Wave (c) $HO_2^- + 2\,e^- + H_2O \rightarrow 3\,OH^-$ (4)

The high current measured at a potential lower than −1.8 V is due to hydrogen evolution from the reduction of H_2O:

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \tag{5}$$

As above, the half-wave potentials were determined via the representation of di/dE against E. The values of $E_{1/2}$ and limiting currents for the observed intermediate steps of O_2 reduction are summarised in Table 2.

The limiting currents for HO_2^- reduction ($i_L^{(c)}$) are lower than the limiting currents for HO_2^- formation ($i_L^{(b)}$) for rotation rates higher than 2000 rpm. This is due to diffusion of the HO_2^- into the aqueous solution where further electrochemical reduction cannot occur.

3.3. *Reduction of EAQ in the two-phase O_2 saturated medium*

The reduction of EAQ in the two-phase medium saturated with oxygen was studied. The concentration of EAQ in the organic phase is 2×10^{-2} M. The voltammogram obtained is presented in the Fig. 1(γ). The reduction of O_2 and EAQ were identified and the waves are attributed to the following reactions:

Wave (a) $O_2 + e^- \rightarrow O_2^{-\cdot}$ (2)

Wave (b) $O_2^{-\cdot} + e^- + H_2O \rightarrow HO_2^- + OH^-$ (3)

Wave (EAQ) $EAQ + 2\,e^- + H_2O \rightarrow EAQH^- + OH^-$ (1)

Wave (c) $HO_2^- + 2\,e^- + H_2O \rightarrow 3\,OH^-$ (4)

The waves (a) and (b) are not so marked in the presence of EAQ. Meanwhile, the di/dE against E relationship demonstrates that the reduction of O_2 proceeds in three steps as expressed by Equations 2, 3 and 4. The half-wave potentials and the limiting currents for all these reactions are summarized in Table 3.

Table 2. Half-wave potentials and limiting currents for the O_2 reduction in the absence of EAQ

Indices (a), (b) and (c) refer to the reduction waves (a), (b) and (c), respectively

Rotation rate	$E_{1/2}^{(a)}$/V	$i_L^{(a)}$/mA	$E_{1/2}^{(b)}$/V	$i_L^{(b)}$/mA	$E_{1/2}^{(c)}$/V	$i_L^{(c)}$/mA
2000	−0.28	−0.04	−0.65	−0.12	−1.57	−0.14
3000	−0.28	−0.07	−0.66	−0.18	−1.58	−0.15
4000	−0.26	−0.09	−0.64	−0.19	−1.5	−0.17
5000	−0.27	−0.09	−0.63	−0.20	−1.49	−0.17

Table 3. Half-wave potentials and limiting currents for O_2 and EAQ reduction in the two-phase medium

(a), (b) and (c) refer to the O_2 reduction waves (a), (b) and (c), respectively
(EAQ) refers to EAQ reduction)

Rotation rate /rpm	$E_{1/2}^{(a)}$/V	$i_L^{(a)}$/mA	$E_{1/2}^{(b)}$/V	$i_L^{(b)}$/mA	$E_{1/2}^{(EAQ)}$/V	$i_L^{(EAQ)}$/mA	$E_{1/2}^{(c)}$/V	$i_L^{(c)}$/mA
2000	−0.31	−0.06	−0.42	−0.08	−1.37	−0.23	−1.54	−0.23
3000	−0.29	−0.06	−0.45	−0.10	−1.38	−0.25	−1.54	−0.25
4000	−0.28	−0.06	−0.46	−0.12	−1.39	−0.28	−1.6	−0.35
5000	−0.29	−0.07	−0.46	−0.14	−1.39	−0.31	−1.59	−0.39

3.4. *Comparison of EAQ reduction in the absence and presence of O_2*

The limiting currents for EAQ reduction are higher in the presence of O_2. The observed current enhancement is about 2 for all rotation rates. This phenomenon can be explained by the following reactions:

$$\mathrm{EAQ} + 2\,\mathrm{e}^- + \mathrm{H_2O} \rightarrow \mathrm{EAQH}^- + \mathrm{OH}^- \tag{1}$$

$$\mathrm{EAQH}^- + \mathrm{O_2} \rightarrow \mathrm{EAQ} + \mathrm{HO_2^-} \tag{6}$$

The reduced form of EAQ, $EAQH^-$, reacts chemically with oxygen to form EAQ near the electrode surface and is then reduced again.

3.5. *Comparison of O_2 reduction in the absence and presence of EAQ*

In the presence of EAQ, the reduction currents for the first and second intermediate reduction steps of O_2 corresponding to waves (a) and (b), referring to Equations 2 and 3, are lower than in its absence. At these potentials, the EAQ reduction can not occur. The decrease in the reduction currents for O_2 is probably due to the coverage of the electrode surface by the organic phase. Thus, the active surface available for oxygen reduction is decreased. For the first wave, (a), the half-wave potentials are slightly shifted towards more cathodic values in the presence of EAQ. On the other hand, the half-wave potentials for the second wave, (b), are shifted towards less cathodic values. The shift is about 230 mV for 2000 rpm and decreases to 170 mV for 5000 rpm. Such a phenomenon was observed in previous studies. The reduction of O_2 took place at a less cathodic potential when compared to that one measured in the absence of EAQ. Shifts in the cathodic peak potentials were observed for the two electron reduction of O_2 in the presence of EAQ on a stationary vitreous carbon cathode in a medium consisting of 1,2-dimethoxyethane (DME) with tetrabutylammonium hydroxide (TBAH) as supporting electrolyte [9]. Several authors attributed this phenomenon to a catalytic effect of EAQ in the reduction of oxygen to hydrogen peroxide [10–12].

For reduction of hydrogen peroxide (wave (c), referring to Equation 4) the measured limiting currents are higher in the presence of EAQ. The observed enhancement of current is about 2 for all rotation rates. Approximately the same multiplication factor was obtained for the current reduction of EAQ in the presence of O_2. Thus, more hydrogen peroxide was produced in the presence of EAQ. The increase in hydrogen peroxide production with addition of EAQ is particularly significant since the direct reduction of O_2 is decreased by an adsorption phenomenon of EAQ onto the vitreous carbon RDE.

3.6. *Charge and mass transfer in the electrochemical reduction of EAQ on the vitreous carbon RDE*

The above results are in good agreement with the ‘wetting mechanism’ observed experimentally by Dworak and Wendt [2], in which the organic droplets penetrate the hydrodynamic boundary layer and are in direct contact with the electrode surface. The mass transfer of the compound in the organic phase is greatly enhanced. Wendt and Feess have distinguished two phenomena which explain this enhancement [4]. Figure 2 describes these two phenomena. The first (Fig. 2(a)) corresponds to a homogeneous dissolution of the organic compound in the aqueous phase followed by diffusion towards the electrode where it is oxidized or reduced. In this case, the charge transfer occurs at the electrode/aqueous phase boundary.

The second phenomenon (Fig. 2(b)) is mass and charge transfer at the electrode/organic phase boundary. EAQ electroreduction on the vitreous carbon RDE in our two-phase medium is closely connected

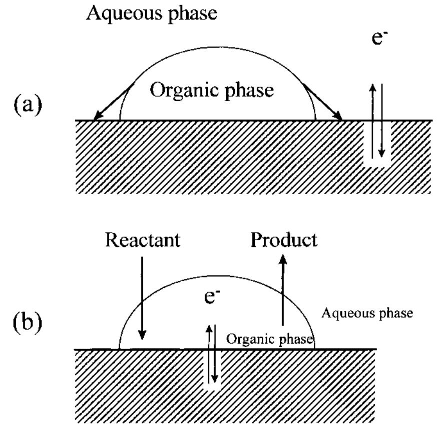

Fig. 2. Schematic representation for the ‘wetting mechanism’ during an electrochemical conversion of a substrate soluble in the two-phase medium’s organic phase according to Feess and Wendt [4].

to the second process. In this mechanism some ionic species are formed in the organic phase which increase the electrical conductivity slightly. The aqueous electrolyte is essential in playing the role of a conductive matrix between the electrodes. The aqueous phase may transfer ions for the neutralization of ionic species which are produced in the organic phase. The aqueous electrolyte can also serve as an extractant for product.

Figure 3 describes the coupled mass and charge transfer involved in the electrochemical conversion of EAQ in the absence of oxygen. The charge transfer occurs at the electrode/organic phase boundary. In the presence of water, the reduction of EAQ is expressed by the following equation:

$$\mathrm{EAQ} + 2\,\mathrm{e}^- + \mathrm{H_2O} \rightarrow \mathrm{EAQH}^- + \mathrm{OH}^- \qquad (1)$$

But in the two-phase medium where the aqueous phase consists of an alkaline solution of sodium hydroxide, the reduced form of the quinone can be extracted in the aqueous phase. The hydroquinone thus produced forms, with Na^+, a disodium salt, $\mathrm{EAQNa_2}$, which is soluble in the aqueous phase where it is extracted. The global equation of the reaction is

$$\mathrm{EAQ_{(org)}} + 2\,\mathrm{e}^- + 2\,\mathrm{Na}^+ \rightarrow \mathrm{EAQNa_{2(aq)}} \qquad (7)$$

During the course of each experiment without oxygen, we clearly observed $\mathrm{EAQNa_2}$ formation by the appearance of a significant red colour in the aqueous phase.

Figure 4 describes the coupled mass and charge transfer involved in the electrochemical conversion of EAQ in the presence of oxygen. Other reactions like direct electrochemical reduction of $\mathrm{O_2}$ or $\mathrm{HO_2^-}$ are not included in this scheme. Charge transfer also occurs at the electrode/organic phase boundary. In the presence of oxygen, the global reaction is

$$\mathrm{EAQ} + 2\,\mathrm{e}^- + \mathrm{O_2} + \mathrm{H_2O} \rightarrow \mathrm{EAQ} + \mathrm{HO_2^-} + \mathrm{OH}^- \qquad (8)$$

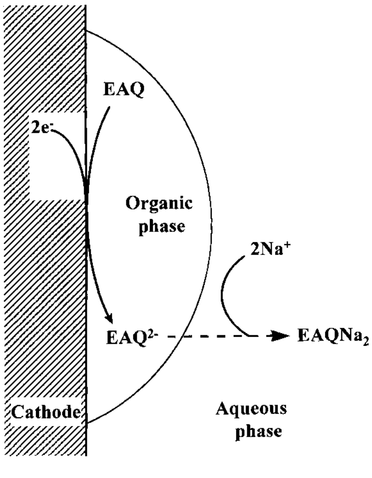

Fig. 3. Schematic representation for the 'wetting mechanism' during the EAQ electroreduction in the two-phase medium TBP/DEB (15/85, vol/vol) and 2 M NaOH in the absence of oxygen on the vitreous carbon RDE. Solid lines refer to electrochemical (charge transfer) or chemical reactions in the two phases; dashed lines refer to mass transfer across the aqueous/organic phase boundary.

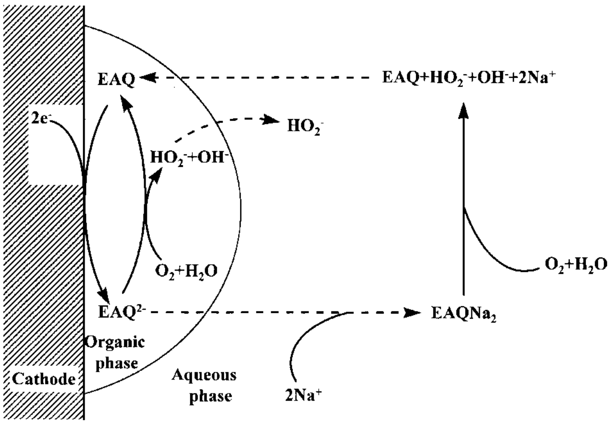

Fig. 4. Schematic representation for the 'wetting mechanism' during the EAQ electroreduction in the two-phase medium TBP/DEB (15/85, vol/vol) and 2 M NaOH in the presence of oxygen on the vitreous carbon RDE. Solid lines refer to electrochemical (charge transfer) or chemical reactions in the two phases; dashed lines refer to mass transfer across the aqueous/organic phase boundary.

Above, we have proposed the following pathway for this reaction:

$$\mathrm{EAQ} + 2\,\mathrm{e}^- + \mathrm{H_2O} \rightarrow \mathrm{EAQH}^- + \mathrm{OH}^- \qquad (1)$$

$$\mathrm{EAQH}^- + \mathrm{O_2} \rightarrow \mathrm{EAQ} + \mathrm{HO_2^-} \qquad (6)$$

It is not possible to exclude another route where the dianion could react directly with the dissolved oxygen in the organic phase:

$$\mathrm{EAQ} + 2\,\mathrm{e}^- \rightarrow \mathrm{EAQ}^{2-} \qquad (9)$$

$$\mathrm{EAQ}^{2-} + \mathrm{O_2} \rightarrow \mathrm{EAQ} + \mathrm{O_2^{2-}} \qquad (10)$$

$$\mathrm{O_2^{2-}} + \mathrm{H_2O} \rightarrow \mathrm{HO_2^-} + \mathrm{OH}^- \qquad (11)$$

After that, the hydrogen peroxide formed could be extracted in the aqueous phase. In the case where the oxygen concentration is insufficient, the formation of the disodium salt cannot be excluded, as in the experiment without oxygen. Thus, the following route can occur:

$$\mathrm{EAQ_{(org)}} + 2\,\mathrm{e}^- + 2\,\mathrm{Na}^+ \rightarrow \mathrm{EAQNa_{2(aq)}} \qquad (7)$$

$$\mathrm{EAQNa_2} + \mathrm{O_2} + \mathrm{H_2O} \rightarrow \mathrm{EAQ} + \mathrm{HO_2^-} + \mathrm{OH}^- + 2\,\mathrm{Na}^+ \qquad (12)$$

During the course of each experiment in the presence of oxygen, the formation of the disodium salt was not observed. The two-phase medium was replenished with enough dissolved oxygen to maintain a very low concentration of this salt. For the experiments in the presence of oxygen, only Equations 1 and 6 or 9, 10 and 11 can be taken into account to explain the mediated formation of hydrogen peroxide by the electrochemical reduction of EAQ.

4. Conclusion

The use of a vitreous carbon rotating disc electrode (RDE) in the two-phase medium has given appropriate conditions for the voltammetric study of quinone dissolved in the organic phase. The electrochemical behaviour of EAQ has been examined in the presence and absence of oxygen. The influence of the presence of EAQ on the electrochemical reduction of O_2 have been studied. It was demonstrated that the production of hydrogen peroxide mediated by the electrochemical reduction of EAQ is feasible. In the presence of EAQ more hydrogen peroxide is produced than by direct reduction of oxygen.

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