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Mediated oxygen reduction at a glassy carbon electrode modified with riboflavin and 9,10-anthraquinones

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Abstract

The electrocatalytic ability for oxygen reduction of a glassy carbon electrode modified with riboflavin and 9,10-anthraquinones (AQNE) is investigated by cyclic voltammetry, chronoamperometry and chronocoulometry techniques. The stability of the modified electrodes is investigated in both acidic and neutral media. The influence of pH on the shift in the oxygen reduction potential and the enhancement in peak current leads to the selection of pH 7.0 as the optimum working value. Combined mediation of 9,10-anthraquinones and riboflavin results in overpotentials that are 592–729 mV lower than that for a plain glassy carbon electrode for reduction of O_2 to H_2O_2. The involvement of two electrons in oxygen reduction is confirmed from chronocoulometric and hydrodynamic voltammetric studies. The heterogeneous rate constants, mass specific current (MSC) and the diffusion coefficients are determined by rotating disc voltammetry.

Keywords: Oxygen reduction; Riboflavin; Modified glassy carbon electrodes; Anthraquinones; Overpotential

1. Introduction

The utilization of modified electrodes in the electrocatalytic reduction of oxygen has assumed significance in recent years because of its importance in electrochemical energy conversion [1–5]. The electrodes have been constructed by immobilization of modifiers at the electrode surface. This facilitates the electron-transfer rate in slow electrochemical reactions. Conventional methods for fixing the mediator to the electrode surface are covalent attachment and entrapment in different matrices. A survey of literature reveals that many mediators such as titanium silicates [6], gold nanoparticles [7], copper [8], ruthenium-iron clusters [9], metal phthalocyanine [10], manganese oxide [11], metal macrocyclic complexes [1,12], pyrimidine bases [13], cobalt-iron oxide nanoparticles [14], cobalt porphyrin [15], palladium alloy [16], and both naphthoquinone [17,18] and anthraquinone [19–22] derivatives have been employed as electrocatalysts for the reduction of oxygen to water or H_2O_2. Numerous studies have been carried out using quinone mediators due to their facile reversible redox behaviour [23–25]. In particular, 9,10-anthraquinones (AQNE) are interesting compounds due to the formation of conductive, electroactive films and monolayers [26], that make them as key constituents, for the modification of electrodes [27]. Salimi et al. [21] studied the catalytic ability of adsorbed 1,4-dihydroxy 9,10-anthraquinone derivatives [21] and 9,10-anthraquinone podands [22] at glassy carbon electrode for the reduction of oxygen. Flavoenzymes are biologically important compounds and take part in the electron transport chain of the respiratory cycle, which involves oxygen reduction. Since riboflavin exhibits facile redox kinetics, it can be used as a good mediator of electrons. In our previous study [17], we reported the catalytic effect of riboflavin and 1,4-naphthoquinone towards oxygen reduction. Little work, however, has been carried out to examine the catalytic properties of the combination riboflavin and anthraquinones. Hence, in the present investigation, glassy carbon electrodes modified with riboflavin and 9,10-anthraquinone, as well as amino derivatives and dyes of the latter material (see Scheme 1),

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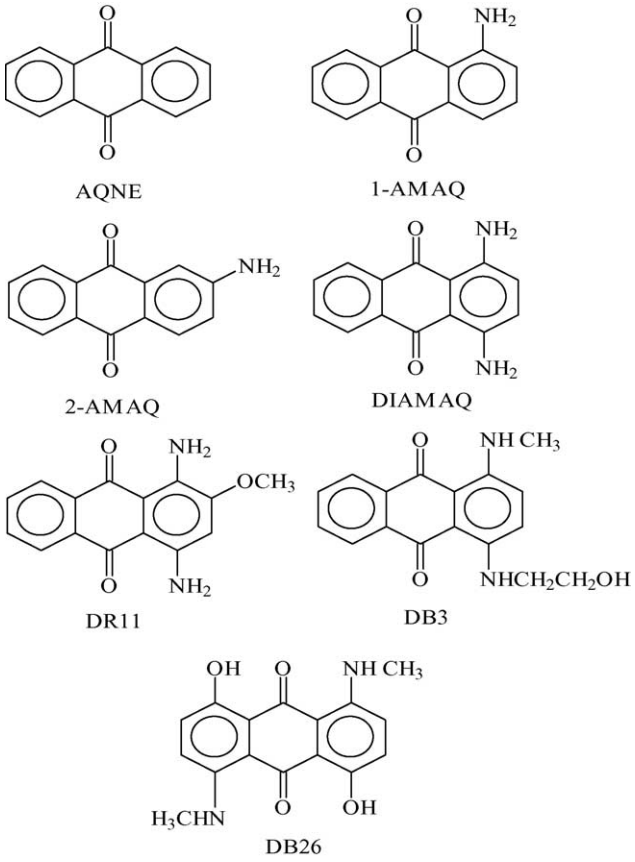

Scheme 1. Structures of anthraquinones.

have been employed. The electrochemical behaviour, stability and efficiency of such modified electrodes for the electrocatalysis of oxygen reduction have been examined by cyclic voltammetry, chronoamperometry, chronocoulometry and rotating disc electrode voltammetry techniques along with determination of diffusional and kinetic parameters.

2. Experimental

2.1. Chemicals

9,10-Anthraquinone (AQNE), 2-amino 9,10-anthraquinone (2-AMAQ), 1-amino 9,10-anthraquinone (1-AMAQ) and 1,4-diamino 9,10-anthraquinone (DIAMAR) were received from Lancaster. Disperse red 11 (DR11), Disperse blue 3 (DB3) and Disperse blue 26 (DB26) were purchased from ATUL India Ltd. and purified before use. Triply-distilled water was de-ionized employing a TKA water purifier and used throughout the experiments. HPLC grade acetonitrile (SRL) was used as received. High purity chemicals available from Merck were used for the present investigation. The aqueous solutions used at different pH were 0.1 M H_2SO_4 (pH 1.0), 0.1M H_2SO_4 + 0.1M NaOH (pH 2.0–3.0), 0.2M CH_3COOH + 0.2M CH_3COONa (pH 4.0–5.0), 0.1M NaH_2PO_4 + 0.1M NaOH (pH 6.0–12.0) and 0.1M NaOH (pH 13.0). The pH of the media was measured using a Cyberscan 500-pH meter. Nitrogen and oxygen gases of 99.999% purity were used during the experiments. Deposition solutions of 4.53×10^{-3} mol dm^{-3} of AQNE, 9.02×10^{-3} mol dm^{-3} of 1-AMAQ, and 5.14×10^{-3} mol dm^{-3} of 2-AMAQ, DIAMAQ, DR11, DB3 and DB26 were prepared, based on their solubility in acetonitrile.

2.2. Electrode preparation

The riboflavin coated glassy carbon electrode (RB/GCE) was prepared by a procedure already reported [28] and the surface coverage of riboflavin was maintained at 2.8×10^{-6} g cm^{-2} in all cases. Then, the RB/GCE was placed in the deposition solutions of anthraquinones at open circuit for varying periods (2–4 h) [29] and the resulting modified electrode (AQ/RB/GCE) was rinsed thoroughly with de-ionized water. A three-electrode cell was employed and comprised a platinum wire counter electrode, a saturated calomel reference electrode (SCE), and the glassy carbon electrode modified with riboflavin and anthraquinone as the working electrode. All electrochemical studies were performed at a thermostatically-controlled temperature of $25.0 \pm 0.1\,^{\circ}$C.

2.3. Apparatus

An EG & G Princeton Applied Research Model 273A potentiostat/galvanostat (Princeton, NJ, USA) controlled by M270 software was employed to perform the cyclic voltammetry, chronoamperometry and chronocoulometry studies. The background current was measured at various sweep rates and subtracted properly in all voltammetric studies. Rotating disc voltammetry was conducted by means of a bi-potentiostat model AFRDE5 with an analytical rotator model AFMSRXE and a MSRX speed model (PINE Instruments, USA).

3. Results and discussion

3.1. Voltammetric behaviour of GC electrodes modified with riboflavin and 9,10-anthraquinones

Voltammograms of the glassy carbon electrode modified with riboflavin and 9,10-anthraquinones at a deaerated condition in different pH media (1.0–13.0) display a single redox couple due to riboflavin and a reversible couple or irreversible cathodic peak depending on the anthraquinone derivative. The influence of sweep rate on the cathodic peak current of anthraquinone reduction was examined to ascertain the nature of the controlling process. The cyclic voltammetric response of 1-AMAQ/RB/GCE at pH 7.0 is given in Fig. 1. The inset shows the linear variation of cathodic peak current of anthraquinone, I_{pc}, with scan rate, ν, which is expected for a diffusionless system. Further, the plot of $\log I_{pc}$ versus $\log \nu$ is a straight line with a slope of around 0.83 and thus confirms

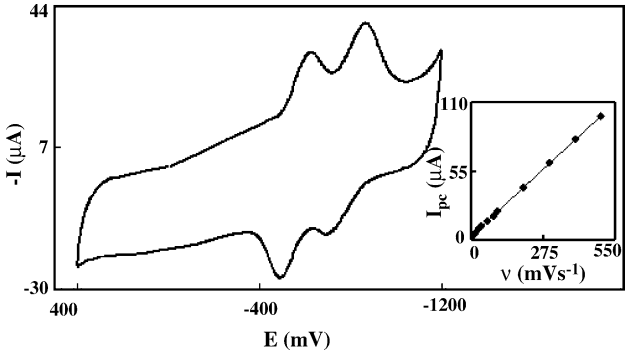

Fig. 1. Cyclic voltammogram for 1-AMAQ/RB/GCE in phosphate buffer, pH 7.0, at 40 mV s^{-1}. Inset shows plot of cathodic peak current vs. scan rate.

the diffusionless process. An increase in peak separation with increase in scan rate confirms the quasi-reversibility of the electron-transfer process. Similar electrochemical behaviour is observed for the other anthraquinone derivatives and dyes.

3.1.1. Effect of pH

Anthraquinones on reduction in aqueous solution yields the corresponding hydroquinone derivatives [21,22]. As the pH of the solution increases, the reduction potentials shift toward more negative values. At the electrode surface, AQNE undergoes a two-electron two-proton reduction to give the hydroquinone (AQH_2) up to pH 8.0 and a two-electron one-proton reduction above pH 8.0 to yield hydroquinone anion (AQH^-). At low pH, the remaining six amino anthraquinone derivatives and dyes undergo two-electron three-proton reduction to give the respective protonated hydroquinones, i.e.,

$$AQNH_2 + 3H^+ + 2e^- \rightarrow H_2AQNH_3{}^+ \quad (1)$$

For DIAMAQ, DR11, DB3 and DB26, the protonation of the second amino group may be difficult because of the presence of electron-withdrawing quarternary ammonium cations in protonated anthraquinones. In the intermediate pH range, the electrode surface reaction is a two-electron two-proton process that leads to the corresponding hydroquinones, i.e.,

$$AQNH_2 + 2H^+ + 2e^- \rightarrow H_2AQNH_2 \quad (2)$$

A two-electron one-proton reduction process occurs at pH > 8.0 to yield the hydroquinone anion:

$$AQNH_2 + H^+ + 2e^- \rightarrow HAQNH_2{}^- \quad (3)$$

Moreover, it is interesting to note that cyclic voltammograms obtained at pH > 9.0 show a dramatic loss in the surface coverage of the electrode and poorly defined peaks. This may be due to either displacement of the adsorbed material by anions that are part of the buffer systems or hydrolysis of the adsorbed anthraquinones at high pH values [21,22].

3.2. Stability of modified electrodes

After immersing the modified electrodes in acidic medium (pH 1.0) for 25 h or in neutral medium for 40 h, cyclic voltammograms were conducted to examine the stability of the electrodes and the reproducibility of their electrochemical behaviour. In both media, a small decrease in the corresponding voltammograms (<5%) was observed. Moreover, there were no measurable changes in the peak height or separation of peaks during 40 min of repetitive scanning between 0 and −1200 mV at pH 7.0 that represented more than 50 complete cycles. The stability of the modified electrodes for oxygen oxidation was also ascertained from the unaltered peak potentials and current observed during 40 min of cycling at 40 mV s^{-1} in the presence of oxygen at pH 7.0. After that scanning, the cyclic voltammogram was run under deaerated conditions and compared with the voltammogram obtained initially in the absence of oxygen. A 3% decrease in the peak height with no change in the separation of peaks was observed. Thus, the reproducibility of the electrocatalytic effect of the modified electrode was confirmed.

3.3. Electrocatalytic dioxygen reduction at surface of modified electrodes

3.3.1. Effect of pH

The electrocatalytic reduction of dioxygen at a GCE modified with riboflavin and anthraquinones was examined in various buffers between pH 1.0 and 13.0. Although the reduction potentials for oxygen and the anthraquinones are pH dependent [21,22], their displacement may be unequal due to the differences in their kinetic behaviour. There is a gradual increase in the cathodic peak current with increase in pH of the buffer solution up to 7.0, for both modified electrodes and a plain GCE. Maximum enhancement of cathodic current and shift in oxygen reduction potential at the modified electrode AQ/RB/GCE led to the selection of pH 7.0 as the optimum condition to investigate the electrocatalysis of oxygen reduction. Salimi et al. [21] also reported pH 6.0–7.0 for this reduction using a GCE modified with 1,4-dihydroxy anthraquinones. The cyclic voltammograms of GCE modified with riboflavin and 1-AMAQ in the absence and presence of oxygen at pH 7.0 are given in Fig. 2. This modified electrode reduces oxygen at two potentials, namely, −310.9 and −672.5 mV. The oxygen reduction at lower potential is probably due to the catalytic effect of the intermolecularly H-bonded complex between riboflavin and 9,10-anthraquinones, and at higher potential result from mediation of the anthraquinones. Since oxygen reduces at −1020.9 mV on a plain GCE, 1-AMAQ combined with riboflavin causes a shift in the oxygen reduction potential (ΔE) of about 710 mV. The observed shifts for different anthraquinones at pH 7.0 are given in Table 1.

By comparing the cyclic voltammograms for oxygen reduction in the absence and presence of anthraquinone derivatives at a RB/GCE, the effect of the anthraquinones alone was examined and the shifts in oxygen reduction potential are also listed in Table 1.

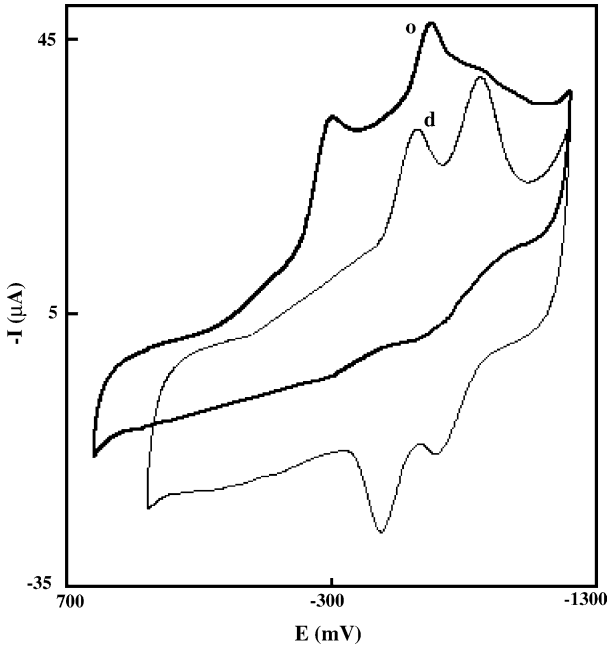

Fig. 2. Cyclic voltammograms of 1-AMAQ/RB/GCE at pH 7.0 in absence (d) and presence of oxygen (o). Scan rate = 40 mV s^{-1}.

3.3.2. Effect of scan rate

Under oxygen-saturated conditions, the variation of cathodic peak current with scan rate was investigated for a GCE modified with riboflavin and anthraquinones. The cathodic peak current, I_{pc}, varies linearly with the square root of scan rate, $\nu^{1/2}$. This indicates that the oxygen reduction process is diffusion controlled.

3.3.3. Effect of substituents

In order to investigate the influence of 9,10-anthraquinone substituents on the electrocatalytic behaviour, the maximum shifts in oxygen reduction potential by the modified electrodes at the optimum pH were compared. The shift is in the order DIAMAQ > DB3 > DB26 > 1-AMAQ > AQNE > 2-AMAQ > DR11. Since the hydrogen-bonded complex formed between anthraquinone and riboflavin catalyses the oxygen reduction, the effect of substituents is discussed in accordance with the stability of the hydroquinone intermediate. The largest shift observed in DIAMAQ is due to the stabilization of the hydroquinone intermediate through intramolecular H-bonding. The presence of inductively electron donating (+I) alkyl groups that increases the electron density at nitrogen in DB3 causes a slight decrease in the strength of the hydrogen bond. But in DB26, the existence of the peri effect on both sides of oxygen in hydroquinone reduces the stability of the intermediate. 1-AMAQ exhibits a smaller shift compared with DIAMAQ, DB3 and DB26 due to the presence of only one intramolecular hydrogen bond between $-NH_2$ and one of the hydroquinone oxygen atoms. The absence of intramolecular hydrogen bonding lowers the stability of intermediates in AQNE and 2-AMAQ. Moreover, the unsymmetrical structure of 2-AMAQ still decreases the shift in oxygen reduction potential. Since the anthraquinone molecules become entrapped in the riboflavin moiety, the symmetry of the catalytic molecule plays a vital role. DR11 exhibits the smallest shift and this is probably due to the steric effect exerted by the ortho substituent $-OCH_3$ and the unsymmetrical structure of the molecule.

3.4. Chronoamperometry

Double potential-step chronoamperometric studies were performed on GCEs modified with riboflavin and 9,10-anthraquinones in the absence and presence of oxygen with an initial and final potential of −100 and −700 mV versus SCE, respectively. As an illustration, chronoamperograms of a plain GCE and one modified by riboflavin and AQNE at pH 7.0 in the presence and absence of O_2 are given in Fig. 3(A) and (B), respectively. By point-to-point subtraction of the background current from the current observed for the modified electrodes in the presence and absence of oxygen, the net current I_{net} was obtained. Under a deaerated condition, the Cottrell plot I_{net} versus $t^{-1/2}$ is a straight line (Fig. 3(C), line d) that extrapolates close to the origin. But in an oxygenated buffer, the corresponding plot (Fig. 3(C), line o) is linear at short time periods, but deviates from linearity at longer times. Extrapolation of the linear part of the plot results in an intercept of 13.01 μA. This transient current appears to be due largely to the catalytic reduction of oxygen by AQNE and riboflavin, since the direct reduction of oxygen at a plain electrode under the same experimental conditions give only

Table 1
Potential shift in oxygen reduction ΔE (CV), number of electrons involved in oxygen reduction n_{O_2} (CC), surface coverage Γ, mass specific current (MSC), heterogeneous rate constant (k), and diffusion coefficient of oxygen D_{O_2} (RDV) for electrocatalytic reduction of oxygen at surface of modified electrodes

AQ	Potential shift ΔE (mV)		n_{O_2}	$10^8\,\Gamma$ (mol cm^{-2})	MSC (A mg^{-1})	$10^{-3}\,k_{O_2}$ (M^{-1} s^{-1})	$10^5\,D_{O_2}$ (cm^2 s^{-1})
	AQ + RB	AQ					
AQNE	705	276	2.10	2.54	0.339	2.88	1.55
1-AMAQ	710	281	1.98	1.30	0.541	2.99	1.41
2-AMAQ	699	270	1.97	3.14	0.262	2.47	1.58
DIAMAQ	729	300	2.04	0.91	0.788	4.66	1.62
DR11	592	163	1.95	5.10	0.139	1.85	1.63
DB3	720	291	2.01	1.56	0.385	3.85	1.58
DB26	714	286	2.14	1.78	0.340	3.10	1.65

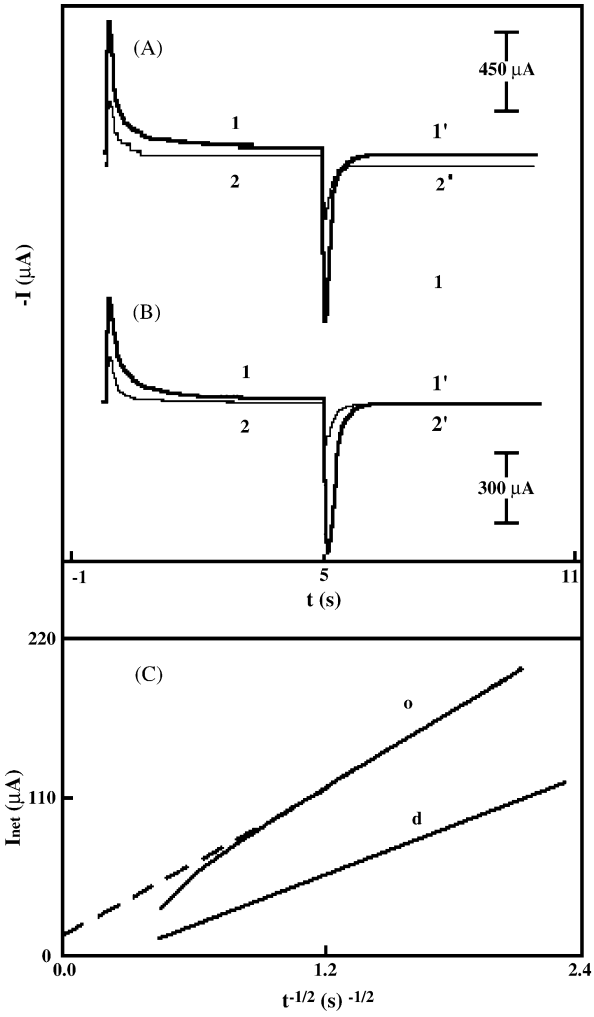

Fig. 3. Chronoamperograms for GCE modified by riboflavin and AQNE at pH 7.0 by double potential-step technique at initial potential of −100 mV and final potential of −700 mV vs. SCE. (A) 1,1′ for modified GCE in O_2-saturated buffer; 2,2′ for plain GCE. (B) 1,1′ for modified GCE in deoxygenated buffer; 2,2′ for plain GCE. (C) Cottrell plot for above modified GCE in (d) absence and (o) presence of oxygen.

a little residual current. The same behaviour is observed for the other anthraquinones.

3.5. Chronocoulometry

The chronocoulometric behaviour of GCEs modified by riboflavin and anthraquinones was examined by the double potential-step technique in the absence and presence of oxygen, with the same initial and final potentials as in the chronoamperometric studies. As an example, Fig. 4 exhibits the chronocoulomogram of GCE modified with riboflavin and DB26. In oxygenated buffer, a large enhancement of charge and the appearance of a nearly flat line on reversal of the potential indicate the irreversible electrocatalytic reduction of oxygen. The same trend was observed for the other anthraquinones. The number of electrons (n) involved in oxygen reduction at the modified electrode is evaluated from the slope of Q versus $t^{1/2}$ plots under oxygen-saturated conditions, using the Cottrell equation, i.e.,

$$Q = 2nFACD^{1/2}\pi^{-1/2}\,t^{1/2} \quad (4)$$

where $C = 1.25$ mM, $A = 0.0314\,\text{cm}^2$ and $D = 1.57 \times 10^{-5}\,\text{cm}^2\,\text{s}^{-1}$. The calculated n values are close to 2.0 and are presented in Table 1. Hence, the reduction product is hydrogen peroxide [17,21,22].

3.6. Rotating disc voltammetry

Hydrodynamic voltammetric studies were also performed on rotating GC electrodes modified with riboflavin and anthraquinones in the absence and presence of oxygen at the optimum pH to determine the kinetic parameters more quantitatively. As an illustration, Fig. 5(A) represents a set of current–potential curves in an oxygen-saturated buffer of pH 7.0 at various angular velocities, ω, with a rotating disk GC electrode modified by riboflavin and DIAMAQ. Curve (a) is the response of the modified electrode in the absence of oxygen. The limiting current, I_l, is defined as the difference between the currents on a modified electrode at the potential corresponding to the diffusion plateau in deaerated and O_2-saturated solutions [17,22]. The Levich and Koutecky–Levich plots are formulated from the limiting currents measured at a potential −950 mV, and are given in Fig. 5(B) and (C), respectively. The Levich plot in Fig. 5(B) is very close to the theoretically calculated line for a two-electron process ($n = 2$) and exhibits a negative deviation at higher ω values. Such non-linearity may be the result of catalytic reduction in which a current-limiting chemical step precedes the electron transfer. This suggestion has been reported earlier [17,21,22]. By contrast, the corresponding Koutecky–Levich plot (Fig. 5(C)) shows a linear relationship between I^{-1} and ω^{-1} with a slope close to that of the theoret-

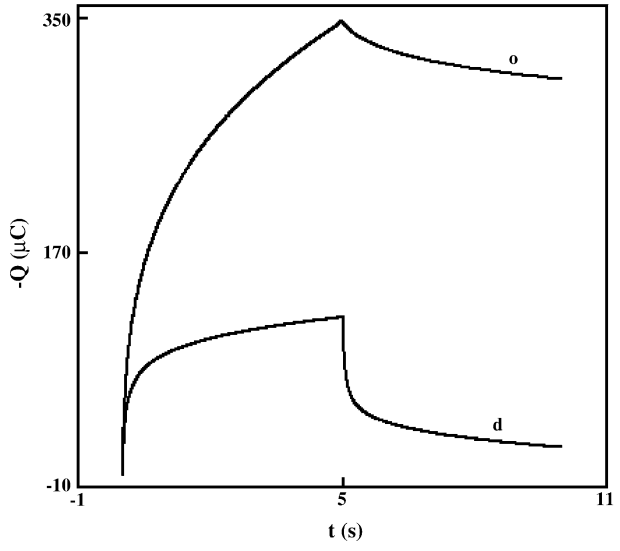

Fig. 4. Chronocoulomogram of DB26/RB/GCE at pH 7.0 in (d) absence and (o) presence of oxygen.

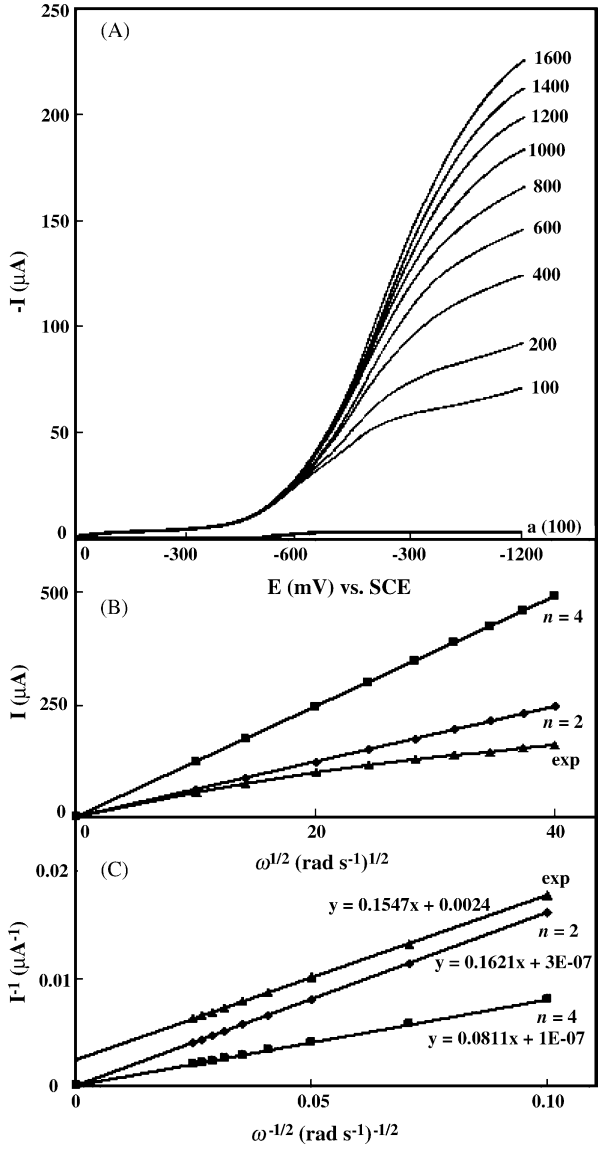

Fig. 5. (A) Current–potential curves for reduction of oxygen (1.25 mM) at rotating glassy carbon electrode modified with riboflavin and DIAMAQ in buffer solution of pH 7.0 at various rotation rates (rpm) and a scan rate of 20 mV s^{-1}. (B) Levich plot of limiting currents at −950 mV (exp), and theoretical Levich plots for two ($n = 2$) and four ($n = 4$) electron reduction of O_2 (C) Koutecky–Levich plots of above data.

ical line for two-electron reduction of oxygen. These findings suggest that adsorbed riboflavin and DIAMAQ sustains the reduction of oxygen to H_2O_2. The same behaviour is observed for the other anthraquinone derivatives. The mass specific activity, or current, of the catalysts (i.e., the current response of the catalyst per mg for oxygen reduction at $\omega = 100$ rpm) was determined [30] and is given in Table 1.

The heterogeneous rate constant for the catalytic oxygen reduction can be evaluated from the intercept of the Koutecky–Levich plot using the expression [17,18,21]:

$$I_1{}^{-1} = I_k{}^{-1} + I_{\text{lev}}{}^{-1} \quad (5)$$

$$I_1^{-1} = [nFAkC_{O_2}\Gamma]^{-1} + [0.62nFAD_{O_2}^{2/3}\eta^{-1/6}\omega^{1/2}C_{O_2}]^{-1} \quad (6)$$

where C_{O_2} is the bulk concentration of oxygen (1.25 mM); ω, the rotational speed; η, the hydrodynamic viscosity (0.01 cm^2 s^{-1}); Γ, the electrode surface coverage of the corresponding anthraquinone; k, the rate constant; all the remaining parameters have their usual meanings. The surface coverage Γ can be evaluated from the equation $\Gamma = Q/nFA$, where Q is the charge obtained by integrating the cathodic peak under the background correction at low scan rate of 10 mV s^{-1}, and the other symbols have their usual meanings. The calculated surface coverage Γ and rate constant values are included in Table 1. The diffusion coefficient of oxygen at rotating modified GC electrodes in oxygen-saturated aqueous buffer was determined employing the Levich equation and are summarized in Table 1.

4. Conclusions

9,10-Anthraquinone, its amino derivatives and dyes have been employed as catalysts for the reduction of oxygen to hydrogen peroxide at riboflavin modified glassy carbon electrodes. Anthraquinones combined with riboflavin exhibit excellent electrocatalytic activities towards oxygen reduction in neutral (pH 7.0) solution at an over-potential that is about 592–729 mV lower than that of a plain GCE. This potential shift is greater than for GC electrodes modified with anthraquinone podands [22] and 1,4-dihydroxy anthraquinones [21]. Values of the heterogeneous rate constant and diffusion coefficient of oxygen are comparable with earlier reports [17,21,22]. Thus, modified electrodes based on a combination of riboflavin and anthraquinones appear promising as oxygen sensors.

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