



Electrochemical study of interaction of the Heavy Metal ions on Redox behavior of Anthraquinone-2-sulphonic acid at the Glassy carbon electrode

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Available online at: www.isca.in, www.isca.me

Received 13th December 2013, revised 16th December 2013, accepted 18th December 2013

Abstract

The electrochemical behavior of anthraquinone-2-sulphonic acid (AQS) and the interaction of the heavy metal ions such as Cu^{2+} , Hg^{2+} , Cd^{2+} and Mn^{2+} at the glassy carbon electrode in the aqueous alcoholic 0.1M KCl solution is studied through cyclic voltammetry technique. The AQS redox system mediated dioxygen reduction process is explained. The scan rate effect of the AQS, Cu-AQS, Hg-AQS, Cd-AQS and Mn-AQS provides useful parameters such as surface concentration of electroactive species, formal potential of the AQS system, rate constant and electron transfer coefficient number. These parameters conclude that the reduction process of AQS is catalysed by manganese ion and oxidation process is catalysed by the cadmium and mercury ions. Multisweep cycle experiment clearly shows the hydroxylation reaction is occurred at the 6th position of AQS in the AQS and metal-AQS systems. The semiquinone formation and stabilized by the OH group in the AQS is clearly explained from the appearance of the peak at -0.3V. Except copper, all the metal-AQS system shows semiquinone peak. Thus copper undergo complexation reaction with 6-hydroxydihydroanthraquinone-2-sulphonic acid which is formed at the reduction process of AQS system after the first cycle.

Keywords: cyclic voltammetry, multisweep cycle experiment, complexation reaction, electrocatalytic activity, hydroxylation reaction.

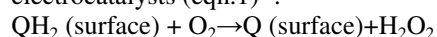
Introduction

Quinones are a series of widespread compounds found in the living organisms performing a variety of biochemical and physiological functions and constitute a broad range of organic compounds with various interesting properties such as antitumor, antibacterial, antifungal and antibiotoxic activities^{1,2}. The main activities of these compounds arise from their reversible electron transfer behaviour. It is also found that, in many cases, the electron transfer process occurs through two one-electron steps via a semiquinone free radical production mechanism³. The 2e- 'peroxide' route is usually obtained on carbon and graphite electrodes, Au, Hg, Ni and some transition-metal macrocycle electrocatalysts⁴.

To enhance the O_2 electroreduction to H_2O_2 at low pH (i.e. < 7) previous research has mainly focused on either electrocatalysis by transition metal macrocycles and surface adsorbed quinone derivatives or electrochemical mediation by bulk quinone compounds. Studies involving various transition metal macrocycle electrocatalysis for O_2 reduction are abundant in the literature. Generally, cobalt macrocycles are most likely to electrocatalyze the 2e- O_2 reduction. Recent research looked at compounds such as electropolymerized cobalt-tetra (O-aminophenyl) porphyrin (poly(CoTAPP))⁵ and cobalt-tetrasulphophtalocyanine (i.e. vitamin B_{12})⁶. Unfortunately, there are several difficulties associated with these electrocatalysts, e.g. loss of stability in the long term, strong pH and electric potential dependence (e.g. vitamin B_{12}) switches from the 2e- to

the 4e- pathway at acid pH) and challenges in preparation of the catalyzed electrode.

Surface-bound quinone or anthraquinone derivatives represent a potential alternative to transition metal macrocycle electrocatalysts (eqn.1)⁷.



This work investigated the electroreduction of O_2 mediated by the anthraquinone sulphonic acid and interaction of the heavy metal ions on the redox behaviour of the anthraquinone sulphonic acid in the aqueous alcoholic 0.1M KCl solution. And the mechanism for the electrocatalytic property of the heavy metal ions on the redox behaviour of AQS acid is studied through multisweep cycle experiment.

Reagents: Anthraquinone-2-sulphonic acid (AQS), ethanol, potassium chloride, copper sulphate, mercurous chloride, cadmium chloride, manganese sulphate

Material and Methods

Electrochemical workstations of CHI, USA: Model 600D with potentiostat driven by electroanalytical measuring softwares was connected to PC computer to perform cyclic voltammetry (CV). An Ag/AgCl (3M KCl) and platinum wire are used as a reference and counter electrode respectively.

Polishing of Glassy Carbon Electrode: The glassy carbon electrode is polished with fine alumina powder (0.3micron) on a wet polishing cloth. To do so a part of the cloth is made wet with deionized water and alumina powder is sprinkled on it. The glassy carbon electrode is then polished on this surface by pressing softly the electrode against the polishing surface in the end for 3-5 minutes. The electrode is then thoroughly washed with deionized water. At this point the electrode surface would look like a shiny black mirror.

Results and Discussion

Scan rate effect: Figure 1 shows the cyclic voltammogram for (A) 0.0034M AQS; (B) 0.0034M AQS+0.001M Cu²⁺; (C) 0.0034M AQS+0.001M Hg²⁺; (D) 0.0034M AQS+0.001M

Cd²⁺; (E) 0.0034M AQS+0.001M Mn²⁺ at different sweep rates in aqueous alcoholic 0.1M KCl solution on glassy carbon electrode. In figure-1(A) has well defined oxidation(A) and reduction(C) peaks. AQS gives larger enhancement in the cathodic peak current, under O₂ saturated condition while the corresponding anodic peak has diminished in its current, clearly showing the electrocatalytic reduction of dioxygen. Here, oxygen reduces at the potential of -780mV. This peak is probable due to the involvement of diffused anthraquinones in dioxygen reduction. The unstable peak observed at -0.6V may be due to the surface bound anthraquinones. Here the cathodic peak current as well as anodic peak currents are increased with scan rate indicating at sufficient overpotentials the reaction is diffusion limited.

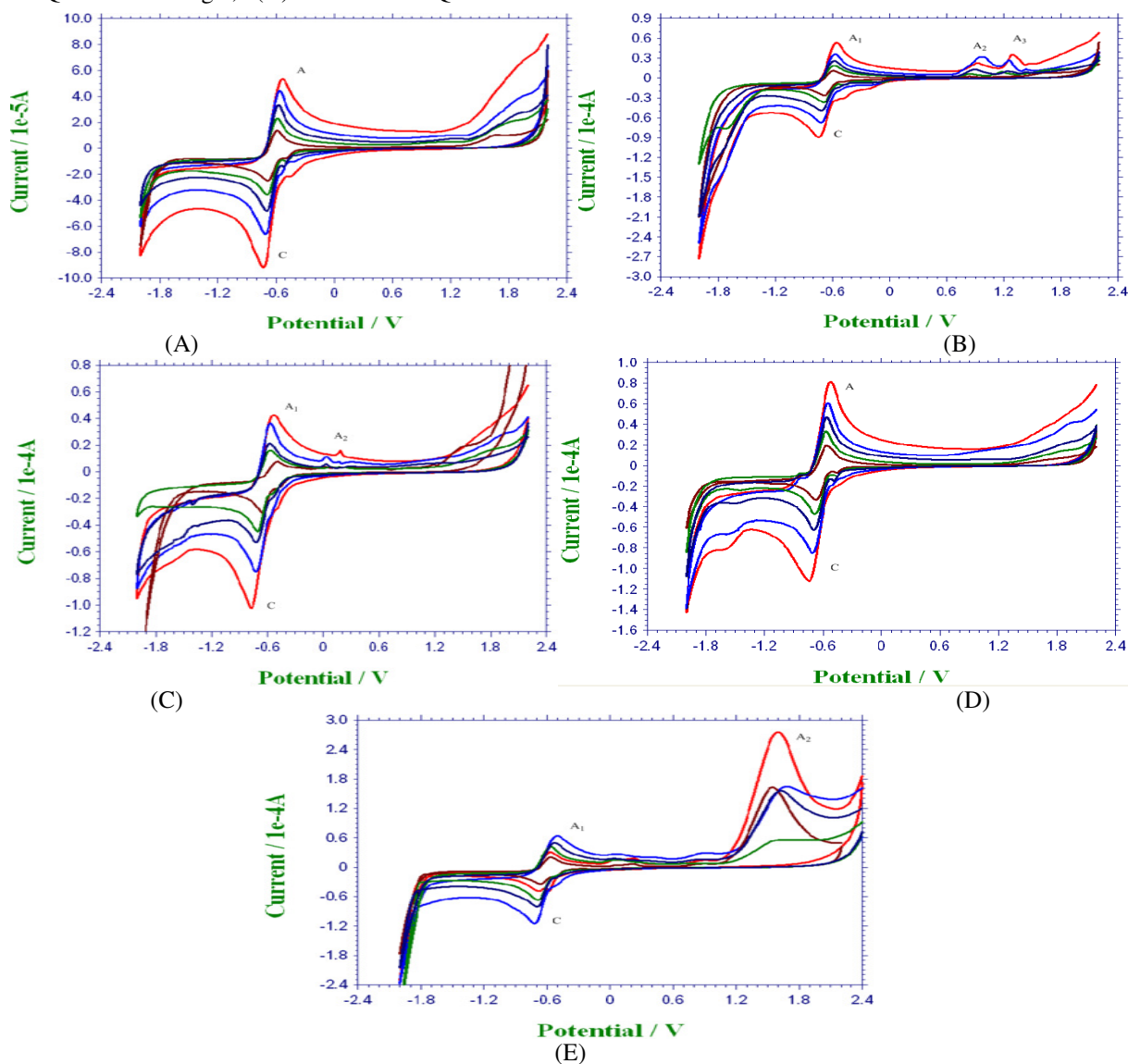


Figure-1

Cyclic Voltammogram for (A) 0.0034M AQS; (B) 0.0034M AQS+0.001M Cu²⁺; (C) 0.0034M AQS+0.001M Hg²⁺; (D) 0.0034M AQS+0.001M Cd²⁺; (E) 0.0034M AQS+0.001M Mn²⁺ at different sweep rates in aqueous alcoholic 0.1M KCl solution on glassy carbon electrode

Table-1

Cyclic Voltammetric parameters for (A) 0.0034M AQS; (B) 0.0034M AQS+0.001M Cu²⁺; (C) 0.0034M AQS+0.001M Hg²⁺; (D) 0.0034M AQS+0.001M Cd²⁺; (E) 0.0034M AQS+0.001M Mn²⁺ at different sweep rates in aqueous alcoholic 0.1M KCl solution on glassy carbon electrode

(A)

Scan rate (mV/s)	I _{pc} x 10 ⁵ (A)	E _{pc} (V)	I _{pa} x 10 ⁵ (A)	E _{pa} (V)
10	-2.575	-0.6842	1.451	-0.5901
20	-3.645	-0.6918	2.375	-0.5818
40	-4.891	-0.6918	3.422	-0.5741
80	-6.679	-0.7072	4.491	-0.5664
160	-9.251	-0.7309	5.416	-0.5274

(B)

Scan rate (mV/s)	I _{pc} x 10 ⁵ (A)	E _{pc} (V)	I _{pa} x 10 ⁵ (A)	E _{pa} (V)
10	-2.719	-0.6842	1.277	-0.5901
20	-3.726	-0.6918	1.974	-0.5818
40	-5.023	-0.7232	2.681	-0.5741
80	-6.857	-0.7232	3.730	-0.5741
160	-9.117	-0.7469	5.506	-0.5504

(C)

Scan rate (mV/s)	I _{pc} x 10 ⁴ (A)	E _{pc} (V)	I _{pa} x 10 ⁵ (A)	E _{pa} (V)
10	-0.3319	-0.6445	1.004	-0.4877
20	-0.4500	-0.7072	1.650	-0.5741
40	-0.5325	-0.7232	2.174	-0.5664
80	-0.7570	-0.7232	3.718	-0.5664
160	-1.029	-0.7699	4.333	-0.5350

(D)

Scan rate (mV/s)	I _{pc} x 10 ⁴ (A)	E _{pc} (V)	I _{pa} x 10 ⁵ (A)	E _{pa} (V)
10	-0.3357	-0.6682	2.007	-0.5587
20	-0.4720	-0.6842	3.404	-0.5664
40	-0.6300	-0.6918	4.762	-0.5587
80	-0.8547	-0.7072	6.258	-0.5504
160	-1.129	-0.7386	8.267	-0.5190

(E)

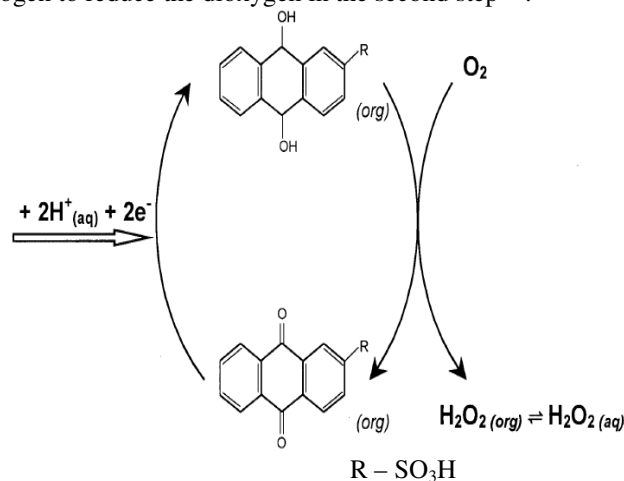
Scan rate (mV/s)	I _{pc} x 10 ⁴ (A)	E _{pc} (V)	I _{pa} ¹ x 10 ⁵ (A)	E _{pa} ¹ (V)	I _{pa} ² x 10 ⁴ (A)	E _{pa} ² (V)
10	-0.3584	-0.6605	2.165	-0.5587	1.642	1.5437
20	-0.5100	-0.6842	3.338	-0.5664	2.775	1.5987
40	-0.6900	-0.6918	4.300	-0.5504	0.5700	1.5987
80	-0.8161	-0.6918	5.083	-0.5274	1.573	1.6301
160	-1.166	-0.7232	6.626	-0.5037	1.660	1.6928

Table-2

Cyclic voltammetric derived parameters for (A) 0.0034M AQS; (B) 0.0034M AQS+0.001M Cu²⁺; (C) 0.0034M AQS+0.001M Hg²⁺; (D) 0.0034M AQS+0.001M Cd²⁺; (E) 0.0034M AQS+0.001M Mn²⁺ at different sweep rates in aqueous alcoholic 0.1M KCl solution on glassy carbon electrode

Compound	Γ _c x 10 ¹¹ (mol/cm ²)	E _c ⁰ (V)	αn _c	k _s ^c (s ⁻¹)	Γ _a x 10 ¹¹ (mol/cm ²)	E _a ⁰ (V)	αn _a	k _s ^a (s ⁻¹)
(A) AQS	0.8077	-0.6824	1.635	7.60 x 10 ²	1.862	-0.5924	1.265	4.001
(B) Cu-AQS	3.109	-0.6902	1.136	6.25 x 10 ²	2.037	-0.5886	2.038	6.539
(C) Hg-AQS	3.420	-0.6747	0.667	3.79 x 10 ²	1.649	-0.5443	2.054	2.548 x 10 ³
(D) Cd-AQS	3.800	-0.6713	1.088	5.52 x 10 ²	2.919	-0.5688	1.86	6.994
(E) Mn-AQS	3.800	-0.6694	1.337	7.01 x 10 ²	2.007	-0.5667	1.19	3.906

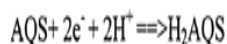
The presence of electron donating substituent's exerting mesomeric effect decreases the stability of hydroquinone moiety obtained in the first step thereby facilitates the availability of hydrogen to reduce the dioxygen in the second step^{4, 8}.



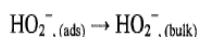
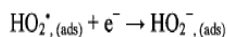
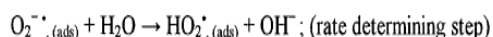
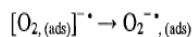
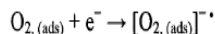
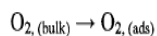
Scheme-1

Dioxygen reduction on the anthraquinone-2-sulphonic acid bound glassy carbon electrode surface

The following equations are described the dioxygen reduction via anthraquinone redox system.



The mechanism of O_2 electroreduction is dependent on many interacting factors besides the composition, such as the bare electrode surface properties and morphology, O_2 adsorption mode, presence of surface active additives, etc. For the electrode material most relevant for the present work, i.e. glassy carbon, the accepted mechanisms for the $2e^-$ reduction of O_2 is^{4, 8}



Where $[O_{2,(ads)}]^{-\bullet}$ and $O_2^{-\bullet,(ads)}$ are two different forms of superoxide adsorbed on the electrode surface.

Cyclic Voltammetric parameters for (A) 0.0034M AQS; (B) 0.0034M AQS+0.001M Cu^{2+} ; (C) 0.0034M AQS+0.001M Hg^{2+} ; (D) 0.0034M AQS+0.001M Cd^{2+} ; (E) 0.0034M AQS+0.001M Mn^{2+} at different sweep rates in aqueous alcoholic 0.1M KCl solution on glassy carbon electrode are tabulated in table.1. The cathodic

peak currents are in the order of Mn-AQS > Cd-AQS > Hg-AQS > Cu-AQS > AQS. The anodic peak current values in the order of Cd-AQS > Mn-AQS > Cu-AQS > AQS > Hg-AQS. One characteristic peak for formation of $Mn(OH)_2$ is appeared at the potential range of 1.5V. But this peak is not observed in the other metal-AQS compounds. This results shows that reduction process is highly catalysed by manganese ions and the oxidation process is highly catalysed by the cadmium ions.

Cyclic Voltammetric derived parameters for (A) 0.0034M AQS; (B) 0.0034M AQS+0.001M Cu^{2+} ; (C) 0.0034M AQS+0.001M Hg^{2+} ; (D) 0.0034M AQS+0.001M Cd^{2+} ; (E) 0.0034M AQS+0.001M Mn^{2+} at different sweep rates in aqueous alcoholic 0.1M KCl solution on glassy carbon electrode are tabulated in table 2. The surface concentration of the electroactive species (Γ) can be estimated according to the following equation⁹.

$$I_p = n^2 F^2 A \Gamma v / 4RT$$

Laviron's equation¹⁰ was used to estimate αn and k_s values, as follows:

$$E_p = E^0 + RT/\alpha nF [\ln(RT k_s/\alpha nF) - \ln v]$$

Where α is the electron transfer coefficient, k_s is the standard rate constant of the surface reaction, v is the scan rate, n is the electron transfer number, and E^0 is the formal potential. Rate constant and αn values can be calculated from the intercept and slope of the linear plot of E_p with respect to $\ln v$, if the value is E^0 is known (plots are not shown). The E^0 value can be deduced from the intercept of E_p vs v plot on the ordinate by extrapolating the line to $v = 0$. Knowing E^0 and from the graphical representations of E_p vs $\ln v$, the values of αn and k_s were obtained from the slope and intercept, respectively.

The surface concentration of electroactive species is in the order of For reduction process: Mn-AQS > Cd-AQS > Hg-AQS > Cu-AQS > AQS

For oxidation process: Cd-AQS > Cu-AQS > Mn-AQS > AQS > Hg-AQS

The transport co-efficient number is in the order of For reduction process: AQS > Mn-AQS > Cu-AQS > Cd-AQS > Hg-AQS

For oxidation process: Hg-AQS > Cu-AQS > Cd-AQS > AQS > Mn-AQS

The rate constant is in the order of For reduction process: AQS > Mn-AQS > Cu-AQS > Cd-AQS > Hg-AQS

For oxidation process: Hg-AQS > Cd-AQS > Cu-AQS > AQS > Mn-AQS

This result suggests that the reduction process is highly catalysed by the manganese ion and oxidation process is highly catalysed by the cadmium ions. In case of oxidation process, manganese-AQS has low values of αn and k_s , because manganese ions are involved in the formation of $Mn(OH)_2$ which is observed from the appearance of characteristic peak at 1.5V.

Multisweep cycle experiment: Figure 2 represents multisweep cyclic voltammogram for(A) 0.0034M AQS; (B) 0.0034M AQS+0.001M Cu^{2+} ; (C) 0.0034M AQS+0.001M Hg^{2+} ; (D) 0.0034M AQS+0.001M Cd^{2+} ; (E) 0.0034M AQS+0.001M Mn^{2+} at 40mV/s in aqueous alcoholic 0.1M KCl solution on glassy carbon electrode. The cathodic peak current for AQS is increased and the oxidation peak current is decreased with increasing scan number in all metal-AQS systems. One oxidation peak appeared at 1.4V suggest that the hydroxylation reaction occurred at the AQS moiety. The negative charge on the sulphonate group is stabilized by resonance and also sulphonate group is a electroinactive group. Thus sulphonate group does not undergo any complexation reaction with metal ions. But in case of Mn-AQS, the redox peaks for the AQS is strongly affected because Mn^{2+} ions react with OH radical to form $\text{Mn}(\text{OH})_2$ on GCE surface. This is confirmed from the appearance of highly enhanced sharp peak at 1.4V. Thus Mn^{2+} ion could be affected the hydroxylation reaction of AQS. In the first cycle of the all the system, the characteristic peak for the semiquinone at the potential of -0.3V is not appeared. The OH group is attached at the 6th position of AQS to form the 6-hydroxyanthraquinone-2-sulphonic acid in the potential range of 1.3V - 1.5V (scheme 2). After the first cycle, semianthraquinone

radical is stabilized by OH present on the AQ moiety and reduced to 6-hydroxy9,10dihydroanthraquinone-2-sulphonic acid which is observed from the clear appearance of the redox peaks. The peak currents for the peaks at -0.3V (semiquinone formation) and 1.4V (hydroxylation) are increased with increasing scan number. Finally 6-hydroxyanthraquinone-2-sulphonic acid is formed. The close appearance of redox peaks for AQS suggest the deposition of 6-hydroxyanthraquinone-2-sulphonic acid on the GCE surface. In case of AQS, Hg-AQS, Cd-AQS, Mn-AQS compounds, the hydroxylation peak is appeared at the potential range of 1.3-1.5V and from the clear appearance of peak at -0.3V, suggest that semiquinone radical is stabilized by the OH group in the AQS acid. But Cu-AQS has broad peak at -1.4V and absence of peak at -0.3V suggest that OH group attached with the AQS moiety undergo complexation reaction with copper. The structure of the complex is shown in fig.3. Because Cu^{2+} ion is a border line acid and easily form complex with OH group. Thus OH group does not stabilize the semiquinone radical in Cu-AQS system. Eventhough Mn^{2+} ion is border line acid, Mn^{2+} does not undergo complexation reaction because Mn^{2+} undergo formation of $\text{Mn}(\text{OH})_2$ on the GCE surface. But Hg^{2+} and Cd^{2+} ions are soft acids and have less complexation effect with OH group.

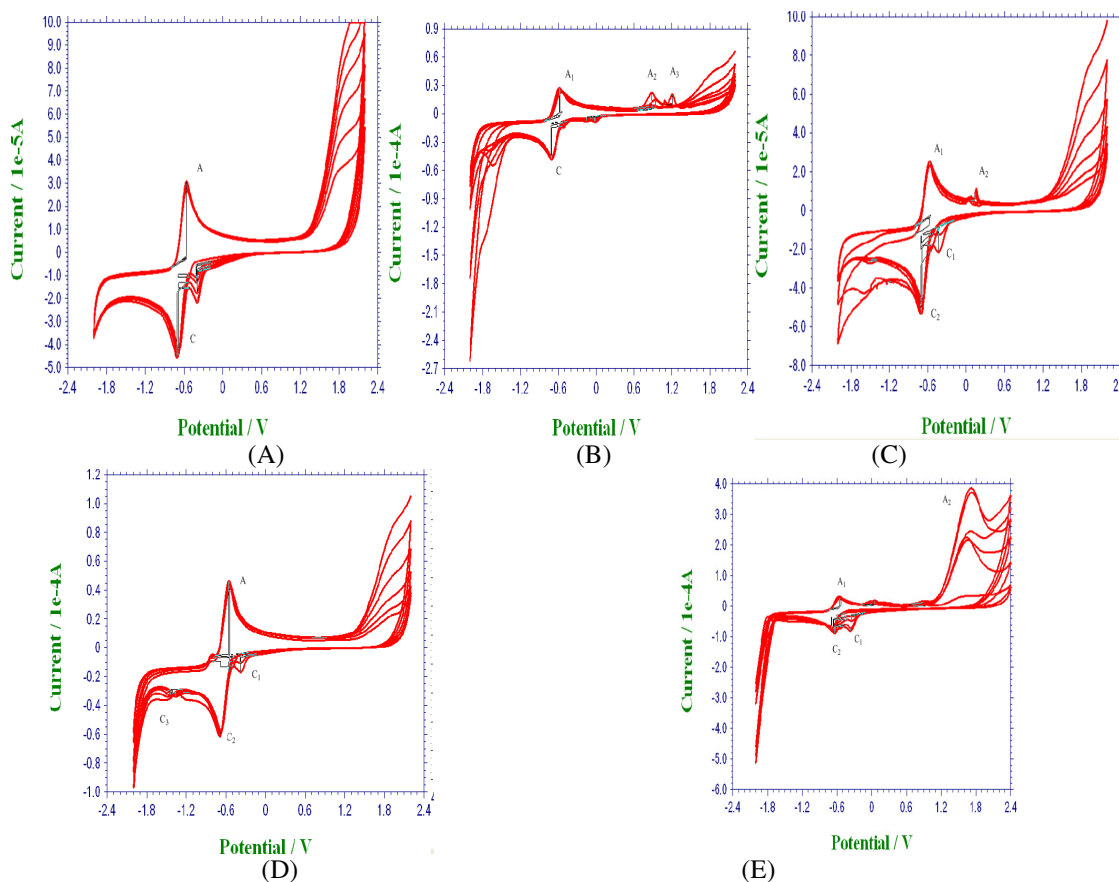
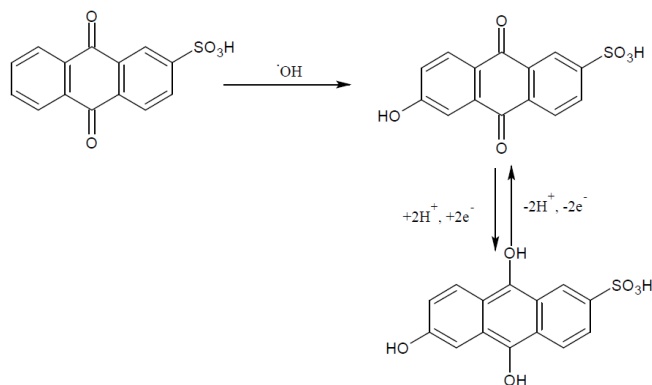


Figure-2

Multisweep cyclic voltammogram for(A) 0.0034M AQS; (B) 0.0034M AQS+0.001M Cu^{2+} ; (C) 0.0034M AQS+0.001M Hg^{2+} ; (D) 0.0034M AQS+0.001M Cd^{2+} ; (E) 0.0034M AQS+0.001M Mn^{2+} at 40mV/s in aqueous alcoholic 0.1M KCl solution on glassy carbon electrode



Scheme-2

Hydroxylation reaction on Anthraquinone-2-sulphonic acid and redox behavior of 6-hydroxyanthraquinone-2-sulphonic acid

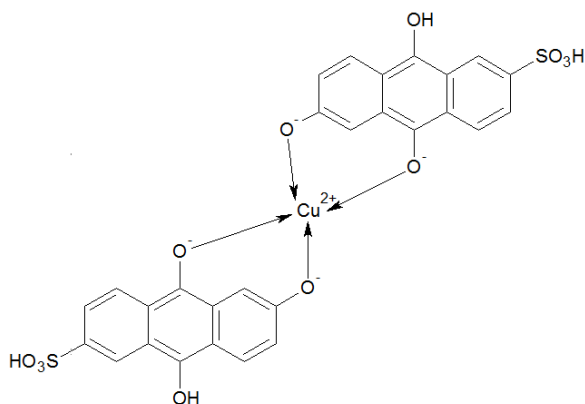


Figure-3

Structure of the bis(6, 10-dioxo-9-hydroxyanthraquinone-2-sulphonic acid)copper(II) ion

Conclusion

The AQS mediated electrolytically reduction of dioxygen process in aqueous alcoholic 0.1M KCl solution produces H_2O_2 and an equilibrium is formed between H_2O_2 in alcohol and H_2O_2 in water. The manganese ion and cadmium ions are highly catalysed the reduction and oxidation process of AQS system respectively. From the multisweep cycle experiment, formation of 6-hydroxyanthraquinone-2-sulphonic acid is confirmed from the characteristic peaks. Only the copper ions undergo complexation reaction with 6-hydroxy 9, 10-dihydroanthraquinone-2-sulphonic acid because Cu^{2+} is a border line acid and is easily form complex with OH group. Semiquinone radical is also stabilized in the Mn-AQS system which suggests that attachment of the OH group at the 6th position of AQS moiety. Mn^{2+} is also a border line acid but

Mn^{2+} ions are involved in the formation $Mn(OH)_2$ and does not undergo the formation of the complex on the GCE surface. Hg^{2+} and Cd^{2+} ions are soft acids and highly catalysed the oxidation process of the hydroanthraquinone which is confirmed from the rate constant values. Thus dioxygen reduction process is highly facilitated by the cadmium and mercury ions.

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