Electrochemical Studies of Amaranth at Surfactant Modified Carbon Paste Electrode: A Cyclic Voltammetry

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Electrochemical reduction of amaranth has been studied at carbon paste electrode in sulphuric acid media using cyclic voltammetric technique. The adsorption of cetyl trimethyl ammonium bromide (CTAB) on a carbon paste electrode was investigated. The results showed that CTAB exhibited two types of adsorptive behavior at a carbon paste electrode at different concentration ranges: monomer adsorption at concentrations below 10 μ L and monolayer adsorption at concentrations higher than 40 μ L CTAB. In the monomer adsorption range, the adsorption of CTAB could effectively reduce the charge transfer resistance and increase the charge transfer rate. However, the surface properties of the carbon paste electrode hardly changed. On the formation of a CTAB monolayer, the structure of the electrode interface changed significantly and the electrode/solution interface. The same mechanism has been proposed for SDS.

Keywords: Adsorption; Amaranth, Carbon paste electrode; CTAB, SDS

1. INTRODUCTION

3-Hydroxy – 4[4-Sulfo-1-napthyl azo] 2,7 Napthalene disulfonic acid, trisodium salt is a pyrazolone dye. It is popularly called as Amaranth dye. This dye is highly water soluble, acidic in nature with M.P. 120^{0} C and molecular formula is $C_{20}H_{11}N_{2}Na_{3}O_{10}S_{3}$ having structure



The molecular structure of amaranth

Amaranth is an azo dye and the redox reaction can takes place at the mercury electrode. The adsorption voltametric behavior of amaranth on a hanging mercury drop electrode has been reported [1]. The electrochemical study of the reaction between albumin and amaranth and its analytical application has been studied by K.Jiao and workers at hanging mercury drop electrode [2].

Surfactants are a kind of amphiphilic molecule with a polar head on one side and a long hydrophobic tail on the other. The applications of surfactants in electrochemistry and electro analytical chemistry have been widely reported [3]. Many of the studies of modified electrodes were undertake simply because electrochemists were curious about new species attached to electrode surface behave compared to these species in solution [4]. Some less soluble surfactants were employed in the immobilization of macro molecules or other functional materials, Wu et al [5] developed a stable multi-wall carbon nanotube (MWNT) modified electrode based on the immobilization of MWNT in the film of insoluble dihexadecyl phosphate (DHP) on a glassy carbon electrode. This electrode exhibited an electro catalytic activity towards biomolecules and has been used as a sensor for the determination of these species [6,7]. Hu's group [8-11] has introduced surfactants to electroanalytical chemistry to improve the detection limits of some biomolecules. The results showed that the electrochemical responses of these compounds were greatly enhanced in the presence of trace surfactants. The applications of surfactant in the immobilization of biomolecules were also reported [12-14]. Chattopadhyay and Mazumdar [15] studied the direct electrochemistry of heme proteins and a neutral surfactant modified glassy carbon electrode. The results showed that the surfactant molecules interacted with the electrode surface in a specific manner and anchored the protein molecules to align in a suitable orientation, which promoted the electron transfer between the protein molecules and the glassy carbon electrode.

Differently from common solid electrodes, such as the glassy carbon electrode and a variety of metal electrodes, the carbon paste electrode, which is made up of adhesives and carbon particles. Generally, the adhesives in carbon paste electrodes are hydrophobic and can accumulate less soluble substrates from solutions to the electrode surfaces via hydrophobic interactions. This accumulation process may be strengthened through the enhancement effects of surfactants on the substrates. Hu and Bard [16] have characterized the adsorption of sodium dodecyl sulfate (SDS) on both charge-regulated and hydrophobic substrates by atomic force microscopy measurement. They found that the interaction between SDS and the positively charged electrode surface was a strong function of SDS concentration, SDS showed different types of adsorptive behaviour on the hydrophobic surface, including the monomer and the monolayer adsorption. Triton X-100 modified carbon paste electrode shows increase in the signal for dopamine [17]. These results were consistent with the conclusions drawn by Montgometry and Wirth [18] using spectroscopic methods.

Electrochemical characterization of cetyltrimethyl ammonium bromide [CTAB] modified carbon paste electrode was studied and mechanism was predicted to show adsorptive behaviour of CTAB on carbon paste electrode [CPE]. They revealed that CTAB formed a compact monolayer on the electrode surface with high density of positive charges directed outside the electrode [13].

As a part of our research work on the electro organic reactions at the surface of the electrodes we extended our work on the modification of carbon paste electrode [19-21, 17].

In this work, the adsorption of CTAB at carbon paste electrode was explored by voltammetry which might be able to explain the enhancement effects of surfactant in electroanalytical chemistry for amaranth. The results revealed not only the adsorptive behaviour CTAB but also the influences of CTAB adsorption on the surface of the electrode interface and the redox reactions in solution. These results might be able to explain the enhancement effects of surfactants in electro analytical chemistry.

2. EXPERIMENTAL PART

2.1. Reagents and Chemicals

Amaranth was dissolved in double distilled water, sulfuric acid (sd Fine). Cetyl tri methyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS) was dissolved in double distilled water. All chemicals were of analytical grade quality and were used with out further purification. The water used was a double distilled. In all the measurements, the supporting electrolyte used was sulfuric acid.

2.2. Apparatus and Procedure

Cyclic voltammetry (CV) was performed on Model EA-201 Electroanalyser (EA-201, Chemilink System). All the experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0mm in diameter), a platinum wire counter electrode and a potassium chloride (KCl) saturated calomel reference electrode (SCE). The carbon paste electrode was prepared as fallows 70% graphite powder and 30% silicone oil were mixed by hand to produce a homogeneous carbon paste. The carbon paste was then packed into the cavity of a homemade carbon paste electrode and smoothed on a weighing paper.



Figure 1. Electrochemical response of Amaranth at a carbon paste electrode in the absence and presence of CTAB.



Figure 2. a) Variation of the logarithm of peak current with the logarithm of the sweep rate for 1mM Amaranth b). Dependence of $i_{pc}/v^{-1/2}$ on log v for peak i_{pc} of 1 mM Amaranth. c) Plot of Ep vs. logarithm of sweep rate of 1mM Amaranth

3. RESULTS AND DISCUSSION

3.1. Electrochemical response of amaranth at carbon paste electrode on to the surface with CTAB.

The electrochemical responses of amaranth at carbon paste electrode were shown in Fig.1 with 60 mM sulphuric acid as supporting electrolyte with 50 mV/s scan rate owing to the complex

properties and the roughness of the electrode surface, the cyclic voltammogram of amaranth in the absence of CTAB is low signal (solid line). However, the voltammetric response is apparently improved in the presence of 60 μ L CTAB, reflected by the enlargement of cathodic peak current (i_{pc}) (dashed line). The probable mechanism is the CTAB surfactant molecule diffuses in to the carbon paste electrode along with the amaranth results increase in the signal. The dependence of the reduction peak current (i_{pc}) as well as peak current function ($i_p/ACv^{1/2}$) on the scan rate showed (v) were studied in the range 50-300 mV/s. A linear relation ship was observed between log i_p and logv (Fig.2a). The plot of $i_p /v^{1/2}$ vs. log v indicated an increase in peak current with an increase in sweep rate (Fig.2b) confirming that the electrode process at the electrode surface has some adsorption. Also, the plot of peak potential (E_{pc}) vs logarithm of scan rate (Fig.2c) was linear with a correlation coefficient of 0.991 and this behavior was consistent with the EC nature of the reaction. [22,23,17]. The electrochemical response of amaranth in the presence of CTAB could be utilized to investigate the adsorptive behaviour of CTAB at a carbon paste electrode, which might be able to explain the enhancement effects of surfactants in some electro analytical systems.

3.2. Effect of concentration of amaranth on to the surface at carbon paste electrode

The supporting electrolyte is 60 mM sulphuric acid with no amaranth in the solution. By adding 10μ L on to the surface the cyclic volatmmogram shows one reduction peak in the forward scan and one oxidation peak in the reverse scan as shown in the Fig.3. The solid line shows supporting electrolyte and dashed line shows 10μ L of amaranth. The concentration of amaranth was varied from 10μ L to 60μ L. The highest current signal was obtained for 40 μ L and then decrease in the current signal for other higher concentration as shown in (Fig.4).



Figure 3. Cyclic voltammogram of the 60 mM sulphuric acid (solid line) and 10μ L of amaranth (dashed line) with scan rate 50 mVs⁻¹.



Figure 4. Effect of concentration of Amaranth on to the surface of the carbon paste electrode.

3.3. Dependence of CTAB adsorptive behaviour on CTAB concentration at a carbon paste electrode

The dependence of the voltammetric responses for 1.0×10^{-3} M amaranth on CTAB concentration was shown in Table 1. Obviously, the addition of CTAB can effectively promote the signals of amaranth even for a trace amount of CTAB. With the increase of CTAB concentration, the peak current increases respectively with the concentration up to 60 µL CTAB concentration. As mentioned above, CTAB might form a monolayer in this concentration range and hence increase in the signal. These results also suggest that completeness of CTAB concentration above 60 µL CTAB. Over the whole concentration range, both the reduction peak current (i_{pc}) increases with the increase of CTAB concentrations.

Table 1. Effect of cetyl trimethyl ammonium bromide surfactant on to the surface of carbon paste electrode at 60 mM sulfuric acid and scan rate = 50 mVs^{-1}

[CTAB] µL	-E _{pc} mV	i _{pa} /μA
0.0	67	30.5
10	80	37.3
20	82	53.3
30	99	60.7
40	110	77.4
50	101	73.5
60	76	53.7

3.4. Electrochemical response of amaranth at carbon paste electrode on to the surface with SDS.

Same type of experiment was carried out with SDS and the electrochemical responses of amaranth at a carbon paste electrode was shown in Fig.5 owing to the complex properties and the roughness of the electrode surface, the cyclic voltammogram of amaranth in the absence of SDS is low signal (solid line). However, the voltammetric response is apparently improved in the presence of 40 μ M CTAB, reflected by the enlargement of cathodic peak current (i_{pc}) (dashed line).



Figure 5. Electrochemical response of Amaranth at a carbon paste electrode in the absence and presence of SDS.

3.5. Electrochemical response of amaranth at carbon paste electrode when CTAB into the solution.

Surfactants even in trace quantities can exert a strong effect on the electrode process. Adsorption of such substances at the electrode may inhibit the electrolytic process, bring about the irregularity in the voltammograms, and shift in the wave to more positive potential [24]. Surface active substances have the common tendency of accumulation at interfaces. The lack of affinity between the hydrophobic portion of the surfactant and water leads to a repulsion of these substances from the water phase as a consequence of oxidation of the microscopic amaranth water interface [25, 26, 27, 19].

These particles thus accumulate at the surface of the electrode and thus decrease the current. Addition of CTAB surfactant results in the shift of E_{pa} towards more negative potential. This may be attributed to the direct adsorption of the surfactants at the carbon paste electrode surface are replaced by the surfactant molecules. At higher concentration of surfactant there was no reduction observed as shown in the [Table-2]

This can be attributed to the adsorption of micellar aggregates on the electrode surface. Decrease in the availability of electro active sites due to solubilisation of the substrate by the micelle may also contribute to this affect [26, 27, 28, 19].

[CTAB]	-E _{pc} mV	I _{pc} μA
μM		
0	67	30.5
0.2	89	22.5
0.5	110	18.2
0.7	135	10.1
0.9	No peak	No peak

Table 2. Effect of cetyl trimethyl ammonium bromide surfactant on cyclic voltammetric data of amaranth at carbon paste electrode at 60 mM sulfuric acid and scan rate = 50 mVs^{-1}

4. CONCLUSIONS

The adsorption of CTAB on a hydrophobic carbon paste electrode surface was investigated by cyclic voltammetry. The results showed that CTAB exhibited different types of adsorptive behavior at carbon paste electrode at different CTAB concentrations. Below 60 μ L, the adsorption of CTAB as the monomer and could effectively affect the charge transfer rate instead of the surface properties of the carbon paste electrode. When the CTAB concentration was higher than 60 μ L CTAB formed a monolayer on the electrode surface, which was completed at 1.0x10⁻⁵ M and resulted in a change of electrode/solution interface as well as the electrochemical behavior of substrates in solution. The same mechanism is also proposed to SDS.

References

- 1. Y.N.Ni, J.L.Bai, L.Jin, Anal. Chim. Acta, 329 (1996) 65.
- 2. W.Sun, K.Jiao, X.Wang and L.Lu, J.Electroanal.Chem., 578(2005) 37.
- 3. J.F. Rusling, Acc. Chem. Res. 24 (1991) 75.
- 4. Allan J. Bard, Journal of Chemical Education, 60 (1983) 302
- 5. K.Wu, J.Fei, S.Hu, Anal.Biochem. 318 (2003) 100.
- 6. Y.Sun, J.Fei, K.Wu, S.Hu, Anal.Bioanal.Chem. 375 (2003) 544.
- 7. K.Wu, J.Fei, W.Bai, S.Hu, Anal.Bioanal.Chem.376 (2003) 205.
- 8. S.Hu, Y.Yan, Z.Zhao, Anal. Chim. Acta, 248 (1991) 103.
- 9. H. Yi, K. Wu, S.Hu, Talanta, 55 (2001) 1205.
- 10. S. Zhang, K.Wu, S.Hu, Talanta, 58 (2002) 747.
- 11. S.Hu, K. Wu, H. Yi, D. Cui, Anal. Chim. Acta, 464 (2002) 209.
- 12. P.Bianco, J.Haladjian, Electrochim.Acta, 42 (1997) 587.
- 13. Wang, N.Hu, J. Colloid interf. Sci., 236 (2001) 166.
- 14. D.Mimica, J.H.Zagal, F.Bedioui, *Electrochem.Commun.*, 3 (2001) 435.
- 15. K.Chattopadhya, S.Mazumdar, Bioelectrochemistry, 53 (2000) 17.
- 16. K.Hu, A.J.Bard, Langmuir, 13 (1997) 5418.
- 17. E. Niranjana, R. Raghavendra Naik, B.E. Kumara Swamy, B.S. Sherigara, H. Jayadevappa, *Int. J. Electrochem. Sci.*, 2 (2007) 923.
- 18. M.E.Mongometry M.J.Wirth, Langmuir, 10 (1994) 861.

- 19. S.R. Murali, B.E.Kumara Swamy, B.S.Sherigara and B.Kalluraya *Bull.of Electrochem.*, 18 (2002) 385.
- 20. A.H.M. Siddalingaiah, S.G.Naik, B.S.Sherigara and B.E.Kumara Swamy. J. of. Mole. Str. (Theochem), 582 (2002) 69.
- 21. G.P.Mamatha, B.S. Sherigara, K.M.Mahadevan and B.E. Kumaraswamy *Bull. of Electrochem*, 21 (2005) 9.
- 22. E.R.Brown, R.F. Large, in: A. Weissberger, B.W. Rossiter (Eds.), *Physical Methods of Chemistry*, Wiley Interscience, Rochester, New York, (1964) 423.
- 23. Rajendra N. Goyal, Vinod K.Gupta, Munetaka Oyama, Neeta Bachheti *Electrochem communications*, 8 (2006) 65.
- 24. J.Herovsky & J.Rute, Principles of Polarography, (Academic Press, New York) 1965.
- 25. R. Jain & S. Gupta, Bull. of Electrochem., 14(2) (1998) 57.
- 26. Y. Shivaraj, J. Ronald Mascarenhas, B.S. Sherigara, B. Kalluraya and R. Sathisha, *Crotia Chimica Acta*, 79 (2006) 273.
- 27. B. Eswarappa, B.S. Sherigara and B.E. Kumara Swamy. Bull. of Electrochem., 20 (2004) 1-6.
- 28. Ronald J. Mascarenhas, A.K. Satpati, Y. Shivaraj, B.S. Sherigara and A.K. Bopiah, *Analytical Sciences*, 22 (2006) 871.

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