Int. J. Electrochem. Sci., 4 **(2009)** 471 - 480

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Studies of Bromothymol Blue at surfactant Modified Carbon Paste Electrode By using Cyclic Voltammetry

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Received: 6 February 2009 / *Accepted:* 19 February 2009 / *Published:* 1 March 2009

The electrochemical response of Bromothymol blue at carbon paste electrode in presence of 0.1M KCl was investigated by the cyclic voltammetric technique. It showed a well-defined oxidation peak at 0.73V and a sensitive reduction peaks at 0.34 V. The effect of concentration and scan rate of Bromothymol blue was studied. The scan rate effect showed the electrode process is adsorption-controlled. The effect of surfactants like Sodium Dodecyl Sulfate (SDS), Cetyltrimethylammonium Bromide (CTAB), and TritonX-100 (TX-100) were studied by immobilizing method. Among these SDS was showed excellent enhancement in both oxidation peak and reduction peak currents. The concentration effect of the SDS surfactant was studied.

Keywords: Bromothymol blue/BTB, SDS, CTAB, TX-100, Carbon paste electrode, cyclic voltammetry

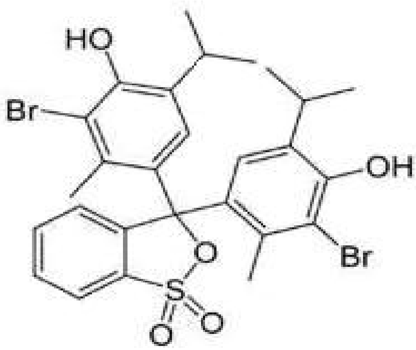
1. INTRODUCTION

Bromothymol blue (BTB) also known as dibromothymolsulfonephthalein is a chemical indicator for weak acids and bases. This Bromothymol blue indicator is known as a probe highly sensitive to the alterations in the structure and physical properties of the proteins[1], phospholipids vesicles [2,3,4] and biomembranes[5,6,7]. The response of Bromothymol blue to the changes of the environmental conditions involves the shift of its protolytic equilibrium. In particulars the dyes binding to the phospholipids vesicles was found to be followed by the increase of the apparent ionization constant (pK_a) [2,3,4]. The effect of methamoglobin on the structure of model membranes composed of phosphatidylcholine diphosphatidylglycerol was studied with the help of pH indicator dye Bromothymol blue [8]

Few literatures are available based on the electrochemical studies on acid-base indicator of anionic nature as a material in the composite electrode [9]. Bromothymol blue is doped with poly-(3, 4-ethylenedioxythiophene) composite electrode was prepared electrochemically by using cyclic voltammetric technique [9]. It is reported to exhibited good stability to immobilize biological material and to get an enhanced electrical signal [10, 11]. The composite electrode selectively detected Cr (VI) from its interference in the presence of a 10-fold x's of Cr (III) and humic acid [9]. The composite electrode material was used recently as a component for electrochromic devices [12], disposable electrodes [13], electronic memories [14], electronic [15] and electrochemical logic circuits [16]

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 [17]. 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 [18]. Some less soluble surfactants were employed in the immobilization of macro molecules or other functional materials, Wu et al [19] 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 [20,21]. Related works have been done by our research group [22-25].

In the present work, the electrochemical behavior of BTB was studied at 0.1M potassium chloride at carbon paste electrode using cyclic voltammetry. The detection of BTB based on the increase in the current signal of oxidation and reduction at bare carbon paste electrode in the presence of three surfactants –viz SDS, CTAB and Triton -X. Among them SDS an anionic surfactant showed current signal more compared to CTAB and Triton-X by strongly adsorbing at the surface of a carbon paste electrode via the hydrophobic interaction. The structure of BTB is as shown in the scheme. 1



Scheme 1. Structure of Bromothymol blue

2. EXPERIMENTAL PART

2.1. Apparatus

Electrochemical measurements were carried out with a model-201 electrochemical analyzer (EA-201 Chemilink system) in a conventional three-electrode system. The working electrode was a carbon paste electrode, having home made cavity of 3mm diameter. A Pt wire and a saturated calomel electrode (SCE) were used as the counter and the reference electrode respectively.

2.2. Reagents

BTB obtained from Sigma dissolved in methanol to prepare 10X10^{-3} M/L standard stock solutions and stored at dark place. SDS, CTAB, TX-100 were dissolved in double distilled water to form 5X10^{-5}M/L solutions. Other chemicals used were of analytical grade except for spectroscopically pure graphite powder. All solutions were prepared with double distilled water.

2.3. Preparation of carbon paste electrode

The carbon paste electrode was prepared by hand mixing 70% graphite powder and 30% silicon oil by hand mixing in an agate mortar for about 30min to get homogeneous carbon paste. This carbon paste was then packed into the cavity of a Teflon tube electrode (3mm in diameter).

Before the measurement modified electrode was smoothed on a piece of transparent paper to get a uniform, smooth and fresh surface.

3. RESULTS AND DISCUSSION

3.1. The electrochemical behavior of Bromothymol blue at carbon paste electrode

The electrochemical response of 1x10^{-3} M BTB at carbon paste electrode was investigated in 0.1M KCl at potential initially sweeps from 0 to 1.0V a well-defined oxidation peak at 0.73V (O_1) in the positive scan and reduction peak at 0.34V (R_1) on the reversal scan are observed in the first cycle (Fig. 1a)

In the second following cycle (Fig; 1b) the peak currents of O_1 and R_1 decrease greatly and a new oxidation peak appears at about 0.46V (O_2). The peak currents of O_1 and R_1 decrease with the increasing of scan number and while those of O_2 gets increases. These results show that the electrochemical behaviors of BTB at carbon paste electrode are totally irreversible and that the products are strongly adsorbed on the electrode surface, blocking the mass transfer BTB from the solution to the electrode surface[8], shown in the (Fig 1b and Fig 1c).

The multiple scan cyclic voltammogram (Fig; 1d) at scan rate 50mV/s from the second scan reveals the decrease in the anodic peak current (O_1) and increase in anodic peak current (O_2) tends to shift the anodic peak potential towards positive side reveals the adsorption of the BTB towards the electrode site and it tells the appearance of new oxidation peak (O_2) may be due to the formation of electroactive species of the oxidized moiety of the (O_1) exhibits the irreversible nature of the compound.

According to Murphy [26], the appearance of O_1 is due to the oxidation of OH on the phenol moiety of BTB. From the structure of BTB it is clear that R_1 may be the reduction peak of bromine atoms on BTB. The O_2 is the electrochemical responses of the product of BTB produced from the oxidation of OH on BTB. (Although the proper electrochemical reactions involved in the oxidation/reduction of BTB have been proposed [27], the hidden relationships between these responses are still unknown). When electrode potential was scanned over the range of 0.5-1.0V, the OH signal (i.e. O_1) is unchanged but no peaks were observed in the reverse scan. Such results prove that reduction of the bromine atoms on BTB is achieved only after the oxidation of OH on BTB because the bromine atoms on the phenol group of BTB are activated after the stable benzene ring is destroyed during the oxidation process.

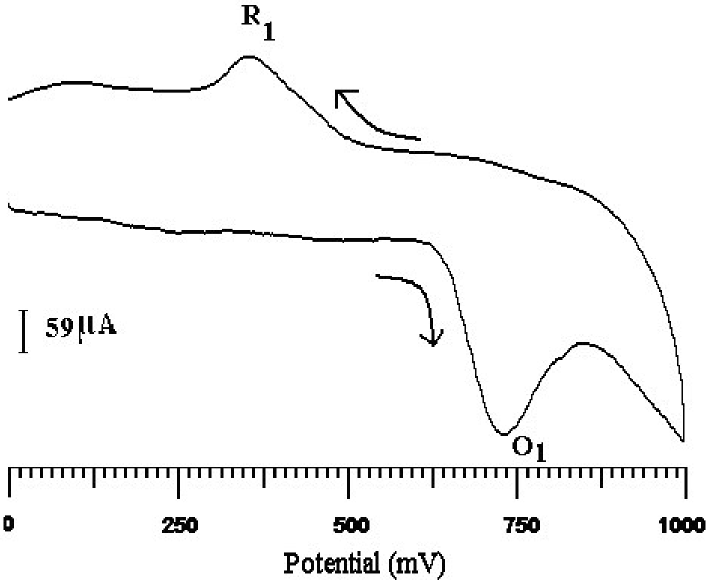


Figure 1a. Cyclic voltammogram of $1X10^{-3}M$ Bromothymol blue at CPE in 0.1M KCL at 50mV/s Scan rate: At first scan

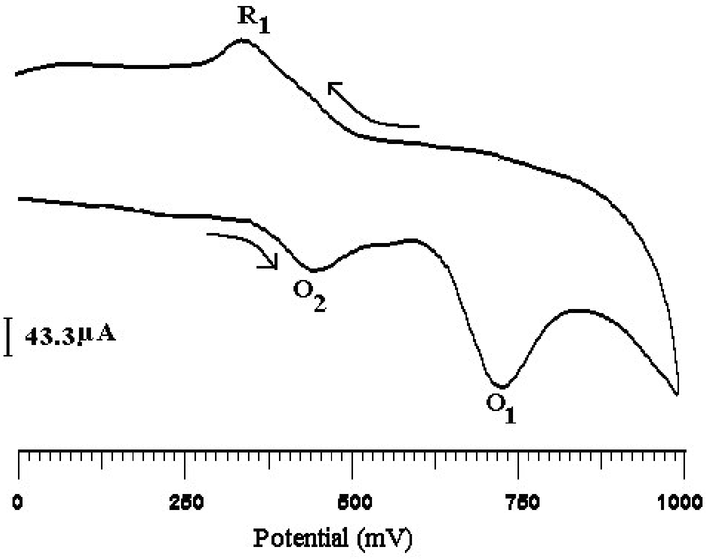


Figure 1b. Cyclic voltammogram of $1X10^{-3}M$ Bromothymol blue at CPE in 0.1M KCL at 50mV/s Scan rate: Appearance of new peak at 0.46V after the first scan

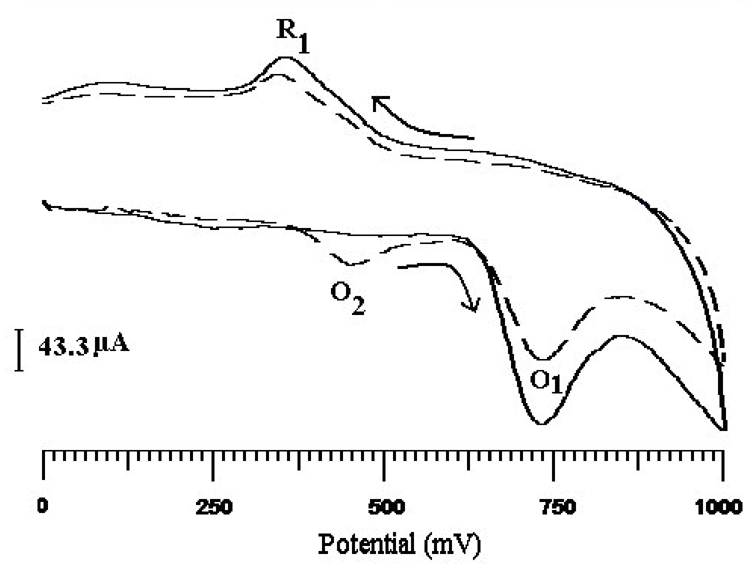


Figure 1c. Cyclic voltammogram of $1X10^{-3}M$ Bromothymol blue at CPE in 0.1M KCL at 50mV/s Scan rate: Comparative Cyclic voltammogram of Fig. (1a) and Fig.(1b)

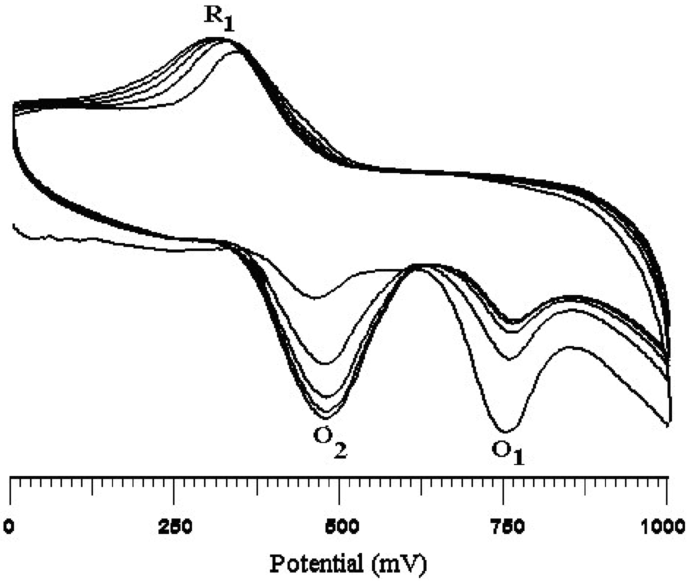


Figure 1d. Cyclic voltammogram of $1X10^{-3}M$ Bromothymol blue at CPE in 0.1M KCL at 50mV/s Scan rate: Multiple Cyclic voltammograms

3.2. Effect of scan rate

The dependence of anodic peak current (i_{pa}) on the scan rate (v) was studied in the range of 25-200mV/s, a linear relationship was observed suggesting the adsorption-controlled process of the BTB (Fig.2a). The plot of i_{pa} v/s scan rate indicate an increase in peak current with an increase in sweep rate

(Fig.2b) confirming that the interface reaction between the electrode and the BTB molecule is adsorption-controlled reaction.

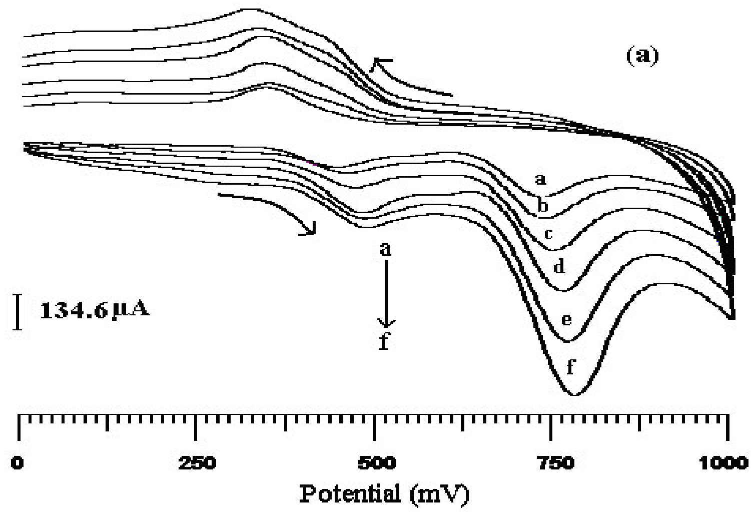


Figure 2a. Cyclic voltammogram of different scan rates (a-f; 25mV/s, 50mV/s, 75mV/s, 100mV/s, 150mV/s, 200mV/s)

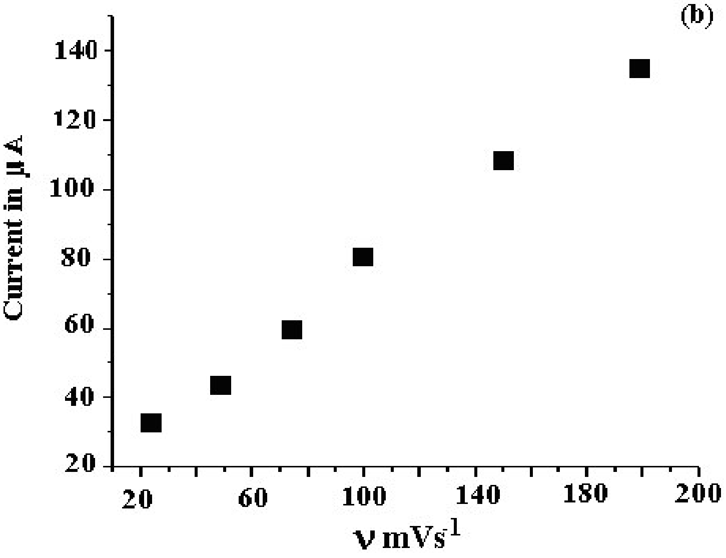


Figure 2b. Plot of anodic peak current v/s Scan rate.

3.3. Electrochemical response of Bromothymol blue at carbon paste electrode in presence of surfactants

Surfactants can be adsorbed on solid surfaces to form surfactant film [28, 29] which may alter the over voltage of the electrode and influence the rate of electron transfer.

Effect of SDS, CTAB and TX-100 surfactants by immobilized forms on the electrochemical response of BTB at carbon paste electrode was investigated.

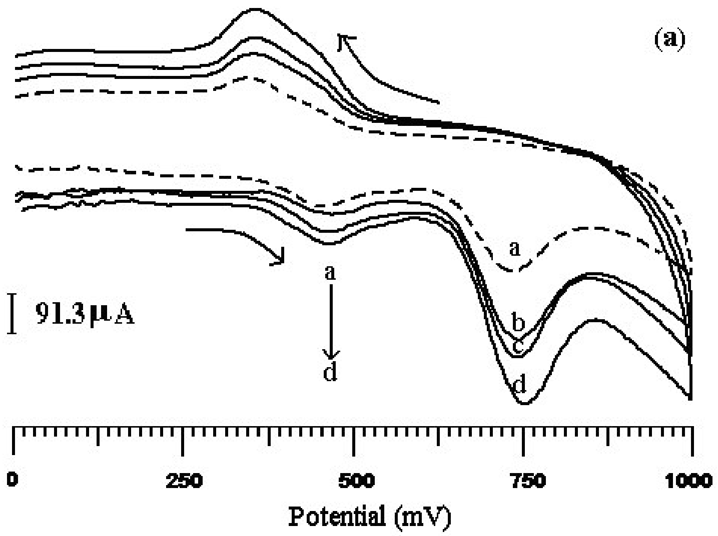


Figure 3a. Cyclic voltammogram of 1X10^{-3}M Bromothymol blue at CPE (a) Bare CPE (b) 5x10^{-5}M CTAB (c) 5x10^{-5}M TX-100 (d) 5x10^{-5}M SDS Surfactant immobilised at carbon paste.

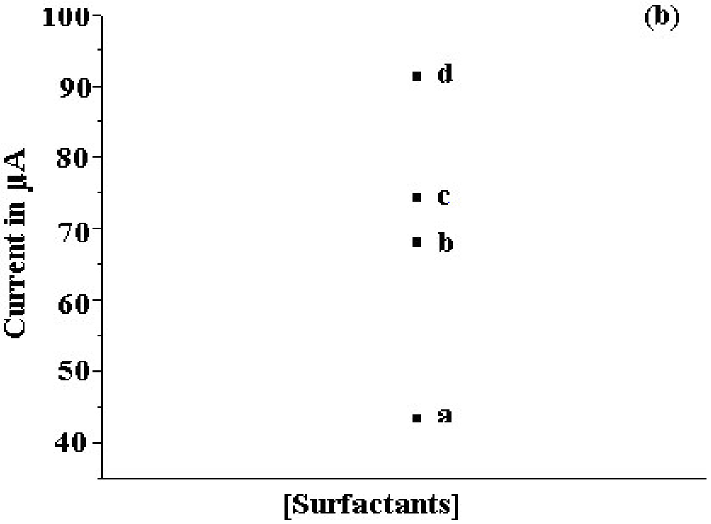


Figure 3b. Graphical representation of current enhancement of 1X10^{-3}M Bromothymol blue (a) Bare CPE (b) CTAB (c) TX-100 (d) SDS

The electrochemical responses of BTB at carbon paste electrode in the presence of trace amount of surfactants surface is immobilized form were studied in 0.1M KCl as supporting electrolyte with 50 mV/s scan rate. The low signal (dotted line) is the cyclic voltammogram of BTB for bare carbon paste electrode. However the voltammetric response is apparently improved in the presence of 4μL of SDS, CTAB and TX-100 (Fig.3a and Fig.3b) in immobilized forms respectively. When the cationic surfactant CTAB and non-ionic surfactant TX-100 were used, there was increase in both oxidation as well as reduction peak currents shifting the cathodic peak potential to the negative side and anodic peak potential to slightly positive and SDS increases current signal more when compared to CTAB and TX-100. These results show that anionic surfactants can more effectively promote both oxidation as well as reduction of BTB

3.4. Effect of SDS surfactant concentration on Bromothymol blue

The effect of surfactant concentration on BTB oxidation and reduction peak currents are shown in Fig.4 for immobilized forms. The peak current increases linearly with the concentration of surfactant at 4μL and again it get decreases increases in concentration above 4μL. The peak potential of oxidation peak (O_1) shifts towards positive side and the peak potentials (R_1) tend to shift towards negative side.

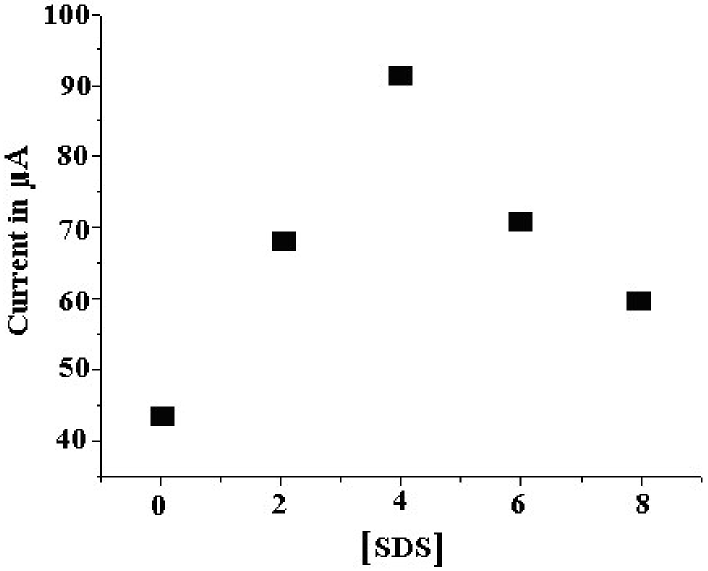


Figure 4. Effect of SDS Surfactant concentration on BTB oxidation peak at (Bare CPE, 2μL, 4μL, 6μL, 8μL) immobilize CPE.

3.5. Effect of Bromothymol blue concentration

The cyclic voltammetric studies showed the successive enhancement of peak current on increasing BTB concentration from 0.5mM to 2.5mM. The plot of peak current v/s the respective concentration of BTB was found to be linear in the range of $0.5X10^{-3}$ M to $2.5X10^{-3}$ M. The variation of anodic peak current (i_{pa}) with concentration shown in the Fig .5

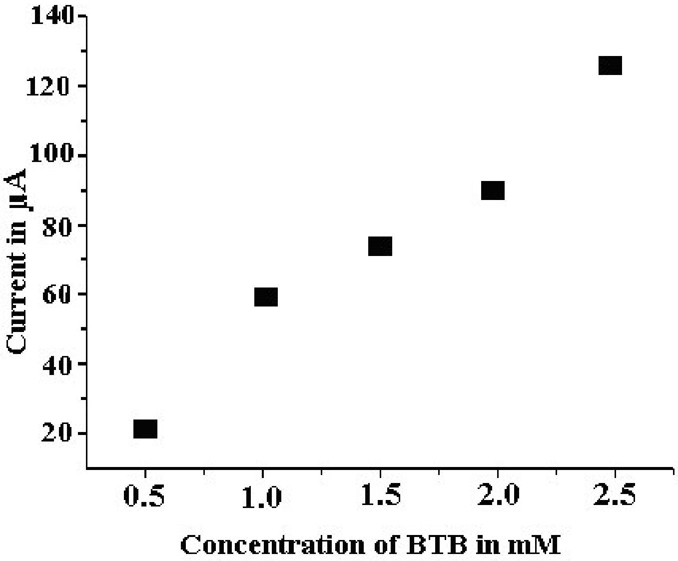


Figure 5. Plot of different concentration of BTB (a-e; 0.5mM, 1mM, 1.5mM, 2mM, 2.5mM).

4. CONCLUSIONS

The electrochemical behavior of BTB was studied at carbon paste electrode by cyclic voltammetry.The anodic peak current increases linearly with the scan rate reveals the adsorption-controlled reaction. The appearance of new anodic peak current at 0.46 mV after the first scan and well growth of its own by suppressing the first anodic peak current reveals the irreversible nature of the Bromothymol blue. This suggests that the overall electrode process is adsorption-controlled. At 4µL SDS surfactant immobilized carbon paste electrode improved the sensitivity of electrode and act as a good sensor.

References

1. E. Antonini, J. Wyman, R. Moretti, A. Rossi-Fanelli, *Biochim. Biophys. Acta*, 71 (1963) 124.
2. G.P. Gorbenko, Ukrain, Biokhim. Zh, *Biochemica et Biophysica Acta*. 63 (1991) 94.
3. T.B. Makarova, N.P. Korolev, B.D. Milgram, I.I. Ivanov, Nauch. Dokl. Vish. Shkol. *Biochemica et Biophysica Acta.* 1 (1983) 34
4. T. Mashimo, I. Ueda, D. Shien, H. Kamaya, H. Eyring, Proc. Natl. Acad. Sci. USA. 76 (1979) 5114
5. R. Colonna, P. Dell'Antone, G. Azzone, *Arch. Biochem Biophys.*, 151(1972) .295
6. J. Jackson, A. Crofts, *Eur. J. Biochem.*, 10(1969) 226
7. P. Mitchell, J. Moyle, L. Smith, *Eur. J. Biochem.*, 4(1968).9,
8. Galina P.Gorbenko.*Biochimica et Biophysica Acta*. 1370(1998)107
9. A.Balamurugan,Zhi-Wei Chen, and She-Ming Chen. *Journal of the Electrochemical Soceity*. 1559 (11) (2008) 151.
10. L. Groenendaal, G. Zotti, P. H. Aubert, S. M. Waybright, and J. R. Reynolds, *Adv. Mater*. (Weinheim, Ger), 15 (2003) 855.

11. L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J. R. Reynolds, *Adv. Mater*. (Weinheim, Ger), 12 (2000) 481.
12. A. A. Argun, A. Cirpan, and J. R. Reynolds, *Adv. Mater*. (Weinheim, Ger.), 15 (2003) 1338.
13. A. Michalska, M. Ocypa, and K. Maksymiuk, *Electroanalysis*, 17 (2005) 327.
14. W. L. Ma, P. K. Iyer, X. Gong, B. Liu, D. Moses, and G. C. Bazan, *Adv. Mater*. (Weinheim, Ger.), 17 (2005) 274
15. S. Moler, C. Perlov, W. Jackson, C. Taussing, and S. Forrest, *Nature* (London). 426 (2003) 166.
16. D. Nilsson, D. Robinson, M. Berggren, and R. Forchheimer, *Adv. Mater*. (Weinheim, Ger.), 17 (2005) 353.
17. J.F. Rusling, *Acc. Chem. Res*. 24 (1991) 75.
18. Allan J. Bard, *Chemical Education*, 60 (1983) 302.
19. K.Wu, J.Fei, S.Hu, *Anal.Biochem*. 318 (2003) 100.
20. Y.Sun, J.Fei, K.Wu, S.Hu, *Anal.Bioanal.Chem*. 375 (2003) 544.
21. K.Wu, J.Fei, W.Bai, S.Hu, *Anal.Bioanal.Chem*.376 (2003) 205.
22. Raghavendra Naik, E. Niranjana, B.E. Kumara Swamy, B.S. Sherigara and H. Jayadevappa, *Int. J. Electrochem. Sci.,* 3 (2008) 1574.
23. Panduranga Char, E. Niranjana, B.E. Kumara Swamy, B.S. Sherigara and K.Vasantakumar Pai, *Int. J. Electrochem. Sci*., 3 (2008) 588.
24. E. Niranjana, R. Raghavendra Naik, B.E. Kumara Swamy, B.S. Sherigara and H.Jayadevappa, *Int. J. Electrochem. Sci*., 2 (2007) 923.
25. Umesh Chandra, Ongera Gilbert, B.E. Kumara Swamy, D. Yadav Bodke and B.S Sherigara *Int. J. Electrochem. Sci.,* 3 (2008) 1044.
26. M.A. Murphy, G.D.Wilcox, R.H.Dahm, and F.Marken. *Electrochem. Commun*., 5 (2003) 51.
27. C. Hu, Q. He, Q. Li, S. Hu, *Anal. Sci*. 20 (2004).
28. S. Hu, Y. Yan, Z. Zhao, *Anal.Chim.Acta*. 248 (1991) 103
29. G.N. Kamau, T. Leipert, S. Shulkla, J.F. Rusling, *J. Electroanal. Chem*. 233 (1987) 173