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Voltammetric Determination of Anthrone Using Cetyl Trimethyl Ammonium Bromide Surfactant Modified Carbon Paste Electrode

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Abstract

In this paper, an electrochemical sensor was developed by Cyclic Voltammetric (CV) technique for the Determination of Anthrone (ANT) by using CTAB (Cetyl Trimetyl Ammonium Bromide) surfactant by immobilizing technique. The electrochemical behavior of ANT was studied at 0.2M PBS (6.5 pH) by CV technique. An enhanced current response has observed for Modified Carbon Paste Electrode (MCPE) towards ANT. Morphology of Bare Carbon Paste Electrode (BCPE) and MCPE were confirmed by Variable Pressure Scanning Electron Microscopy (VPSEM). The electrode process was adsorption controlled. Under optimum condition linear calibration plot of ANT was obtained from 3×10^{-5} M to 5×10^{-5} M and 6×10^{-5} M to 1.7×10^{-4} M with the detection limit of 21×10^{-7} M and limit of quantification of 7×10^{-6}M. The modified electrochemical sensor was easy to fabricate, sensitive and having good stability.

Keywords: Anthrone; Cyclic Voltammetry; Electrochemical Determination; Electrochemical Sensor

Introduction

Anthrone is an aromatic ketone [1]. It is widely used as in the colorometric determination of carbohydrates, and it is widely used as a laxative. ANT can cause respiratory irritation; long term exposure may result in disease of airways involving difficult breathing and related systematic problems. Over the last decades biosensor related research has shown a dramatic growth. The action of surfactants in electroanalytical field has been widely reported [2-18] and was widely used which will increase the electron transfer and also improve the detection limit of biologically active molecule. With increasing the use of ANT, it became an important to develop a simple, reliable, sensitive and simple cost analytical method for the determination of ANT. During the past decades' scientists are focused to developing Voltammetric methods for the detection of electroactive species. Cyclic voltammetry [19-21] is a simple, powerful, widely used method in electrochemical studies, and which has been widely used to investigate the electrochemical properties of the species which are electroactive in nature. After invention of many of the new material a need has been expressed for developing of stable simple and efficient material as sensors for the determination of electroactive species by electrochemical method. At present, whole area of research occupied with developing of new material and fabrication of new electrochemical sensors.

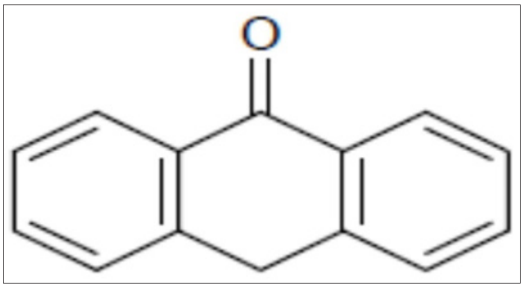

Figure 1: Structure of ANT.

Chemically modified electrode [22] has got an important application in medicine and pharmaceutical analysis. In electroanalytical research determination of electroactive species by voltammeric method become the major target. Carbon Paste Electrode (CPE) [23] has been widely used as working electrode in the electrochemical application because of simple preparation, easy renewal, low cost and is more compatible with biological tissues. Because of all these advantages of CPE, become the suitable substrate for the preparation of modified electrodes. In the present work, we developed a suitable sensitive and selective chemically modified electrode for determination of ANT. Here, we describe CV and Differential Pulse Voltammetry (DPV) studies of ANT. There is no work has reported on the determination of ANT by Cetyl Trimethyl Ammonium Bromide Modified Carbon Paste Electrode (CTABMCPE) and the structure (ANT) is shown in Figure 1.

Materials and Methods

Chemicals

CTAB was purchased from Molychem India Pvt. Ltd. Graphite, Silicone oil, Anthrone was obtained from Nice Chemicals, India and stock solution of ANT was (25×10^{-4} M) was prepared in acetone. 25×10^{-3} M CTAB was prepared in distilled water. Monosodium hydrogen phosphate and disodium hydrogen phosphate was received from Merck specialties Pvt. Ltd. Phosphate buffer solution was prepared by mixing 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 and buffer solution having different pH values prepared by mixing appropriate amount of Na_2HPO_4 and NaH_2PO_4. All the experiments are carried out under room temperature (25 ± 1 °C) and distilled water was used to prepare all the solution.

Electrode Preparation

BCPE was prepared as mixing 70% graphite powder and 30% silicone oil in agate mortar for about 20 minute to get a homogeneous paste. This carbon paste was packed in to a teflon tube cavity having 3mm diameter. The electrochemical contact was setup with a copper wire contact to the paste. Before placing the electrode for measurements, it was smoothed on a tissue paper to get uniform and smooth surface. CTABMCPE was made by immobilizing 10 µL CTAB on the surface of the electrode for 5 minute.

Instrumentation

All the electrochemical experiment was carried out using a potentostat (EA-201 electroanalyser, Mumbai, India). A conventional three - electrode set up with the CTABMCPE and BCPE as working electrode, Pt wire as counter electrode and saturated calomel electrode (SCE) as reference electrode was used for the electrochemical measurements. A personal computer was used for data storage and processing. All the potential is measured versus the SCE.

Result and Discussion

Effect of CTAB Concentration

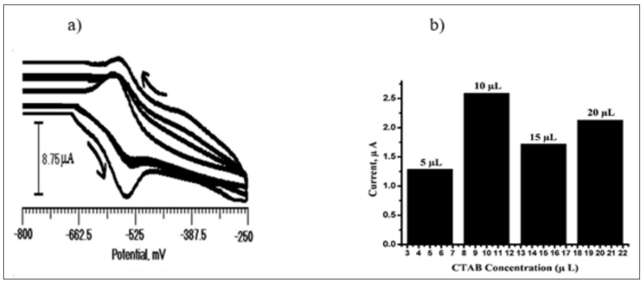

Figure 2: Cyclic voltammogram of 2×10-4 M ANT at BCPE with different concentration of CTAB, 5 µL to 20 µL in 0.2 M PBS (6.5 pH) at the scan rate of 100 mV/s, (b) Oxidation peak current Vs CTAB concentration.

Figure 2a shows the relationship between concentration (5 µL, 10 µL, 15 µL, 20 µL) of CTAB and peak current of ANT. CTAB exhibits a remarkable enhancement of peak current of ANT. Peak current has increased by increasing the concentration of CTAB up to 10 µL but after 10 µL it has observed that the peak current was decreasing. The amount of CTAB modifier was optimized as 10µL for the best voltammogram and was chosen for the experiment. The dependence of the oxidation peak current of ANT on different concentration were drawn and shown in Figure 2b.

Morphology Studies

BCPE and CTABMCPE were characterized by VPSEM. Figure 3 shows the typical VPSEM image of BCPE (a) and CTABMCPE (b). The surface of BCPE was irregularly arranged with the graphite. But it can be seen that there is a uniform arrangement of Surfactant molecule CTAB on the surface of the carbon paste electrode. From the VPSEM image it is clear that the carbon paste electrode was coated by surfactant, which will lead to improve the surface properties CTABMCPE.

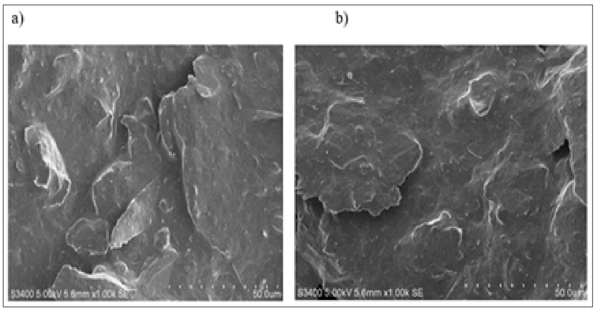

Figure 3: VPSEM image.
Note:
a) BCPE,
b) CTABMCPE

Electrochemistry of ANT

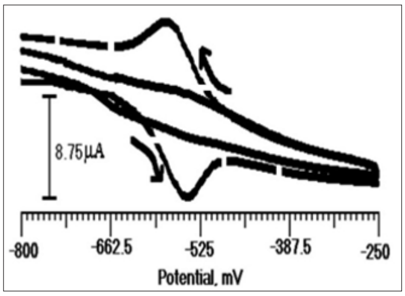

Figure 4: Cyclic voltammogram of CTABMCPE with ANT (2×10^{-4} M) (dashed line) and without ANT (solid line) in 0.2 M PBS, pH 6.5 at the scan rate of 100 mV/s.

In order to know the electrocatalytic activity of ANT on CTABMCPE, cyclic voltammetric response were obtained at 0.2 M PBS (pH 6.5) in the absence (solid line) and presence (dashed line) of 2×10^{-4} M in the potential range -800 mV to -250 mV, and data were shown in Figure 4. There is no redox peak was observed in the absence of ANT, and there is a drastic enhancement of anodic peak current (E_{pa} = -543 mV and I_{pa} = -2.59 µA) and cathodic peak (E_{pc}

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= -575 mV and I_{pc} = 12.77 μA) obtained by the addition of $2×10^{-4}$ M ANT which indicates that the electrochemical response of ANT improved at CTABMCPE in other word electrocatalytic activity of ANT has increased at CTABMCPE.

Voltammetric Behavior of ANT at CTABMCPE

Figure 5 shows the cyclic voltammogram of ANT (2×10-4 M) at CTABMCPE (dashed line) and BCPE (Solid line) at 0.2M PBS (pH 6.5). A well-defined redox peak was observed for ANT at CTABMCPE (-543 mV (E_{pa}) and -575 mV (E_{pc})), compared with BCPE (no peak was observed). On this observation, it is clear that surfactant improves the catalytic effect of ANT, which will lead to the enhancement of peak current. The peak current obtained for CTABMCPE is much larger than compared to BCPE.

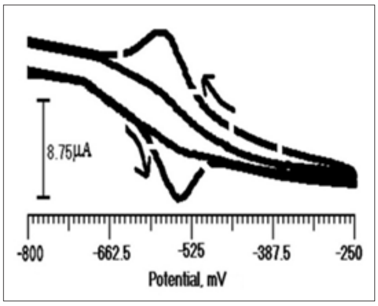

Figure 5: Cyclic voltammogram of ANT ($2×10^{-4}$ M) in 0.2 M PBS buffer solution of pH 6.5 at BCPE (solid line) and CTABMCPE (dashed line).

Effect of Scan Rate on Peak Current of ANT

The effect of potential scan rate on peak current of ANT at CTABMCPE at 0.2 M PBS (pH 6.5) was investigated in order to study the reaction mechanism. Figure 6a shows the effect of scan rate and peak current relation in the range of 100 mV/s to 300 mV/s. It has been seen that the peak current linearly increased with the increase of the scan rate and shows the electrode process was adsorption-controlled process, with s linear equation of Ipa= -5.59+ 0.088 v (mV/s) with a correlation coefficient (R) of 0.99534 (Figure 6b).

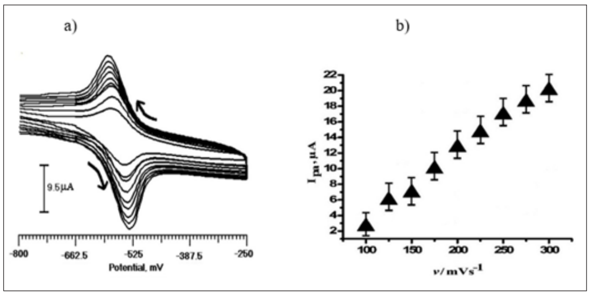

Figure 6:
Note:
a) Cyclic voltammogram of ANT ($2×10^{-4}$ M) at CTABMCPE in pH 6.5 at various scan rates from 100 to 300 mV/s
b) Plot of peak current of ANT as a function of scan rate.

Effect of pH on Peak Current of ANT

The effect of pH on the CTABMCPE for the determination of ANT was investigated in the range 6.0 to 8.0 using 0.2 M PBS at the scan rate of 100 mV/s by CV (Figure 7a). It was observed that with increase of pH the peak current was shifted to less negative direction and maximum value obtained at pH 6.5, in order to get good sensitivity and selectivity, 6.5 pH was taken as optimum value (Figure 7b). The plot of anodic peak potential Vs pH (Figure 7c) exhibited a linear relationship with a regression equation of, E_{pa} (mV) = 160.6+59.6 pH with a correlation coefficient of 0.9976 From the slope 59.6 mV/pH it is clear that the value is close to the theoretical value 59 mV/pH shows that number of protons and electrons involved in the reaction of ANT oxidation are equal.

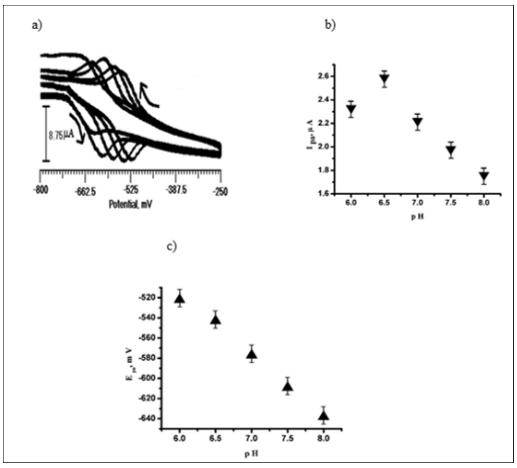

Figure 7:
Note:
a) Cyclic voltammogram at CTABMCPE in 0.2 M PBS in different pH values
i. 6.0
ii. 6.5
iii. 7.0
iv. 7.5
v. 8.0 containing ANT ($2×10^{-4}$ M),
b) anodic peak current (Ipa) Vs pH,
c) Epa Vs pH.

Electrochemical Determination of ANT by DPV

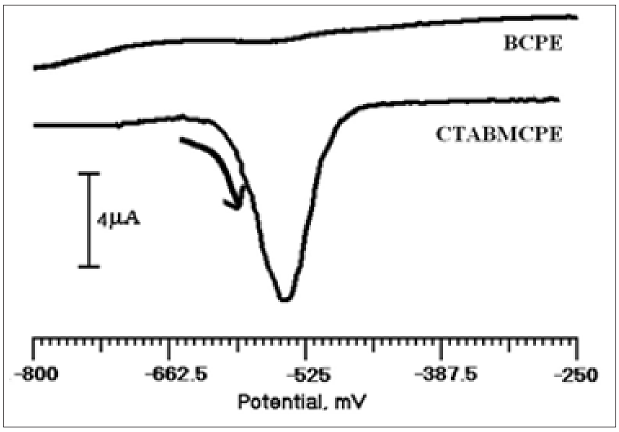

Figure 8: DPV of a solution containing ANT (2×10-4 M) in 0.2 M PBS at the BCPE and CTABMCPE.

DPV gives better resolution and higher current sensitivity than CV. Figure 8 shows the DPVs obtained of $2×10^{-4}$ M ANT in 0.2 M

PBS (pH 6.5) at the scan rate of 50 mV/s for BCPE and CTABMCPE. For BCPE a peak current (-1.97 µA) was observed at -556 mV and higher peak current (-13.32 µA) which has observed at -545 mV for CTABMCPE. The peak current obtained for the CTABMCPE which 7 times is higher than the value obtained for the BCPE, shows the good electrocatalytic effect of ANT at CTABMCPE.

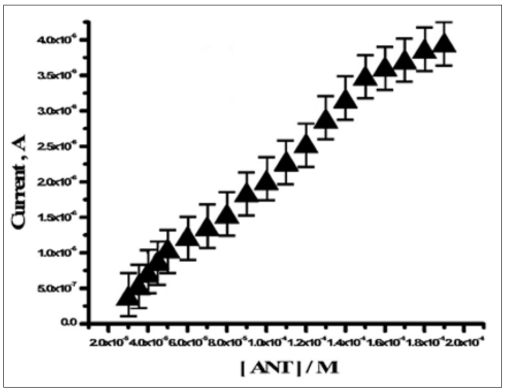

Figure 9: Calibration plot for the determination of ANT at the CTABMCPE in pH 6.5 PBS with the scan rate 100 mV/s.

Repeatability and Stability Studies

The stability and reproducibility of the modified electrode was investigated under optimum condition. For 6 successive measurements of ANT (2×10^{-4} M) with the same electrode relative standard deviation was observed as (RSD) 3.9 %, which indicates that the good repeatability of the method. Stability of the modified electrode was measured by 35 consecutive cycles and it was observed that even after 35 cycles 93 % of initial current signal was retained, which shows that the modified electrode having good stability. These properties will make the modified electrode attractive in the analytical field.

Calibration Plot and Limit of Detection

Calibration curve for ANT at the CTABMCPE was characterized by CV under optimum condition. Figure 9 shows the CV of ANT with various concentrations in PBS (0.2 M) at CTABMCPE. ANT shows two linear segment in the range of 3×10^{-5} to 5×10^{-5} M and 6×10^{-5} to 1.7×10^{-4} M and corresponding linear regression equation was Ipa (A)=$-6.72\times10^{-7}+0.033C$ (M) (R=0.999) and Ipa (A)=$-4.03\times10^{-7}+0.024C$ (M) (R=0.995). The Limit of Detection (LOD) and Limit of Quantification (LOQ) of ANT were calculated by using following formulas, LOD = 3S/M and LOQ = 10S/M [24]. Where S is the standard deviation and M is the slopes obtained from the calibration plot and were obtained as 21×10^{-7} M and 7×10^{-6} M respectively.

Conclusion

In summary, a simple, sensitive method has been developed for the determination of ANT by CV. This method was simple and less time consuming than other methods. CTABMCPE exhibits a good electrocatalytic activity to ANT oxidation compared to the bare electrode. The electrochemical behavior of the CTABMCPE strongly depends on the solution pH. Modified electrodes show a good sensing performance, good repeatability and also have good stability. Apart from these sensor exhibited a low detection limit (21.1×10^{-7} M).

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References

1. Finar IL (2009) Organic chemistry (6th edn). Pp. 966.
2. Manjunatha JG, Deraman M, Basri NH, Mohd Nor NS, Talib IA, et al. (2014) Sodium dodecyl sulfate modified carbon nanotubes paste electrode as a novel sensor for the simultaneous determination of dopamine, ascorbic acid, and uric acid. Comptes Rendus Chimie 17(5): 465-476.
3. Manjunatha JG (2017) Surfactant modified carbon nanotube paste electrode for the sensitive determination of mitoxantrone anticancer drug. J electrochem Sci Eng 7: 39-49.
4. Teradale AB, Lamani SD, Ganesh PS, Kumara Swamy BE, Das SN (2017) CTAB immobilized carbon paste electrode for the determination of mesalazine: A cyclic voltammetric method. Sensing and Bio- Sensing Research 15: 53-59.
5. Lihong L, Chunfeng W, Zhuo K (2016) Cetyltrimethylammonium Bromide (CTAB)-Ionic liquid composite modified electrode for sensitive cyclic voltammetric determination of bisphenol A. Chemical Research in Chinese universities 32(6): 992-995.
6. Ramya Kumari CT, Mamatha GP, Santhosh HM (2016) Voltammetric detection of trimethoprim at CTAB modified carbon paste electrode. Chem Sci Trans 5(3): 619-626.
7. Manjunatha JG, Deraman M (2017) Graphene paste electrode modified with sodium dodecyl sulfate surfactant for the determination of dopamine, ascorbic acid and uric acid. Anal Bioanal Electrochem 9(2): 198-213.
8. Manjunatha JG, Kumar Swamy BE, Ongera Gilbert, Mamatha GP, Sherigara BS (2010) Sensitive voltammetric determination of dopamine at salicylic acid and TX-100, SDS, CTAB modified carbon paste electrode. Int J Electrochem Sci 5(5): 682-695.
9. Teradale AB, Lamani SD, Das SN (2016) Up growth effect of cetyl trimethyl ammonium bromide with carbon paste electrode for the electrochemical determination of allopurinol and its biological activities. Anal and Bioanal Electrochem 8: 814-829.
10. Ramalakshmi N, Muthukumar S, Marichamy B (2013) Electrochemical study of Mn^{2+} redox system on 4-hydroxybenzylidene-Carbamide-CTAB modified glassy carbon electrode. Res J Chem Sci 3(8): 29-37.
11. Das DK (2008) Electrochemical determination of Zn^{2+} ion using diphenylamine/single walled carbon nanotube/cetyltrimethylammonium bromide modified glassy carbon electrode. Journal of Surface Science and Technology 24: 149-162.
12. Sanjeevaraddi RS, Nandibewoor ST (2011) Voltammetric-oxidation and determination of 5-Flurouracil and its analysis in pharmaceuticals and biological fluids at glassy carbon electrode mediated by surfactant cetyl trimethyl ammonium bromide. Der Pharma Chemica 3: 253-265.
13. Yang C, Ping ping X (2007) Studies on enhanced oxidation of estrone and its voltammetric determination at carbon paste electrode in the presence of cetyltrimethylammonium bromide. Bulletin of the Korean Chemical Society 28(10): 1729-1734.
14. Raoof JB, Hosseini SR, Mousavi Sani SZ (2015) Improved hydrogen evolution on glassy carbon electrode modified with novel Pt/cetyltrimethylammonium bromide nanoscale aggregates. Chinese Journal of Catalysis 36(2): 216-220.

15. Lowinsohn D, Bertotti M (2008) A Biosensor based on immobilization of lactate oxidase in a PB-CTAB film for FIA determination of lactate in beer samples. J Braz Chem Soc 19(4): 637-642.
16. Zou J, Guo M, Feng Y, Yang M, Cao Y, et al. (2017) Voltammetric determination of nonylphenol using a glassy carbon electrode modified with a nanocomposite consisting of CTAB, Fe_3O_4 nanoparticles and reduced graphene oxide. Microchimica Acta 184(2): 533-540.
17. Ramalakshmi N, Muthukumar S, Marichamy B (2013) Preparation and characterization of 4-hydroxybenzylidencarbamide-CTAB modified glassy carbon electrode by using $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox system. International Journal of Chemical and Physical Sciences 2(4): 16-24.
18. Lu Q, Zhang W, Wang Z, Yu G, Yuan Y, et al. (2013) A facile electrochemical sensor for nonylphenol determination based on the enhancement effect of cetyltrimethylammonium bromide. Sensors 13: 758-768.
19. Bard AJ, Faulkner LR (2008) Electrochemical methods: Fundamentals and application: pp. 856.
20. Grosser DK (1993) Cyclic voltammetry: Simulation and analysis of reaction mechanism: pp. 154.
21. Kalcher K (1990) Chemically modified carbon paste electrode in voltammetric analysis Electroanalysis 2(6): 419-433.
22. Svancara I, Schachl K (1999) Testing of unmodified carbon paste. Chem Listy 93: 490-499.
23. Manjunatha JG (2017) Electroanalysis of estriol hormone using electrochemical sensor. Sensing and Bio-Sensing Research 16: 79-84.
24. Manjunatha JG (2018) A novel poly (glycine) biosensor towards the detection of indigo carmine: A voltammetric study. Journal of Food and Drug Analysis 26(1): 292-299.

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