Research Article

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 Trimethyl 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 $3 \times 10^{-5}$ M to $5 \times 10^{-5}$ M and $6 \times 10^{-5}$ M to $1.7 \times 10^{-4}$ M with the detection limit of $2 \times 10^{-7}$ M and limit of quantification of $7 \times 10^{-6}$ 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 colorimetric 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 voltammetric 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 \((25\times10^{-4}\text{M})\) was prepared in acetone. \(25\times10^{-4}\text{M}\) 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 \(\text{Na}_2\text{HPO}_4\) and 0.2 M \(\text{NaH}_2\text{PO}_4\) and buffer solution having different pH values prepared by mixing appropriate amount of \(\text{Na}_2\text{HPO}_4\) and \(\text{NaH}_2\text{PO}_4\). All the experiments are carried out under room temperature \((25 \pm 1 ^\circ \text{C})\) 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 into 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 potenstat (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

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 \(2\times10^{-4}\text{M}\) in the potential range \(-800 \text{mV} \text{ to } -250 \text{ mV}\) 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_{\text{pa}} = -543 \text{ mV} \text{ and } I_{\text{pa}} = 2.59 \mu \text{A}) and cathodic peak \((E_{\text{pc}} = 753 \text{ mV} \text{ and } I_{\text{pc}} = 2.59 \mu \text{A})\).
= -575 mV and $I_{pc} = 12.77 \mu A$) obtained by the addition of $2 \times 10^{-4}$ 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 ($2 \times 10^{-4}$ 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.

**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 a linear equation of $I_{pa} = -5.59 + 0.088 v$ (mV/s) with a correlation coefficient (R) of 0.99534 (Figure 6b).

**Electrochemical Determination of ANT by DPV**

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

**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.

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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.

**Repeatability and Stability Studies**

The stability and reproducibility of the modified electrode was investigated under optimum condition. For 6 successive measurements of ANT (2×10⁻⁷ 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 3×10⁻⁷ to 5×10⁻⁵ M and 6×10⁻⁵ to 1.7×10⁻⁴ M and corresponding linear regression equation was \( \text{Ipa (A)} = -6.72×10^{-7} + 0.033 \times \text{M} \) (R=0.999) and \( \text{Ipa (A)} = -4.03×10^{-7} + 0.024 \times \text{M} \) (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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