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The Electrooxidation of Tetracycline at Acetylene Black Electrode in the Presence of Sodium Dodecyl Sulfate

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Abstract: The electrooxidation of tetracycline (TC) at acetylene black electrode has been studied in the presence of sodium dodecyl sulfate (SDS). Tetracycline (TC) exhibited very sensitive oxidation peak in this system. The peak current was proportional to TC concentration, and the detection limit was 1.2×10^{-8} mol/L. The system was used to the determination of TC in pharmaceuticals.

Keyword: Tetracycline, surfactant, sodium dodecyl sulfate, acetylene black electrode.

Tetracyclines are widely used as broad-spectrum antibiotics in human and veterinary medicine. Numerous studies have been devoted to the development of sensitive methods for measuring tetracyclines. Electrochemical method was also used to detect tetracyclines[1]. However, the electrooxidation of tetracycline is rarely reported. In this paper, the anion surfactant sodium dodecyl sulfate (SDS) is successfully used to investigate the electrooxidation of tetracycline (TC). TC exhibits very sensitive oxidation peaks at the acetylene black electrode in the presence of SDS. The proposed method has been applied for the determination of TC in pharmaceuticals, and the results compared favorably.

Electrochemical measurements were performed on a CHI 830 electrochemical analyzer (Chenhua Co., Shanghai). The acetylene black working electrode was prepared by mixing 10 mg acetylene black and 15 µL paraffin oil to form a homogeneous acetylene black mixture. The mixture was pressed into the cavity of the electrode body, and the electrode surface was smoothed manually on weighting paper.

Figure 1 shows the oxidation of TC at the acetylene black electrode in pH 2.5 Mcllvaine buffer solution (0.2 mol/ L Na_2HPO_4 - 0.1 mol/ L citric acid). The oxidation peak of TC is flat as 1×10^{-6} mol/ L TC is added into the buffer solution (curve a). And that no oxidation peak appears as only 1×10^{-4} mol/ L SDS existed (curve b). However, a remarkable oxidation peak of TC is obtained in the presence of TC and SDS (curve c). Surfactants can be adsorbed on solid surfaces to form surfactant film[2,3], which may alter the overvoltage of the electrode and influence the rate of electron transfer. In acid media, the dimethyamino substituent on position four of TC is easy to be positively charged by protonation. In the present case, adsorption of the anionic surfactant SDS at the electrode

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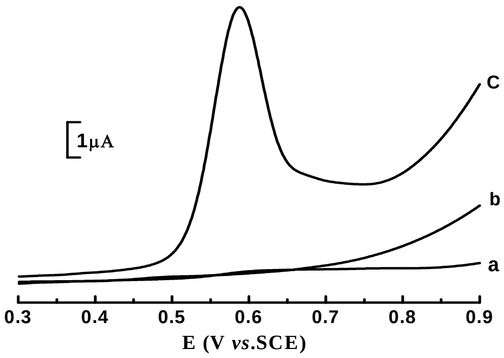
surface may form a negatively charged hydrophilic film on the electrode. This negatively charged hydrophilic layer increased the concentration of the protonated TC on the electrode surface *via* electrostatic interaction, the overvoltage was reduced and the electron transfer rate was increased. So it was the synergic interaction of the adsorption of SDS and the protonated TC that facilitated the oxidation of TC at the acetylene black electrode. As the accumulation potential shifted, the peak current of TC had no obvious change, indicating that the adsorption of SDS was independent on the charge of the surface of the electrode. This also showed it was the long hydrocarbon tail of SDS adsorbed on the surface of the electrode, which was consistent with the above expatiation.

Figure 1 Voltammograms of an acetylene black electrode in Mcllvaine buffer solution (pH 2.5):



a. in the presence of TC; b. in the presence of SDS; c. in the presence of TC and SDS. Scan rate: 100 mV/s; Open circuit; Accumulation time: 150 s; TC: 1×10^{-6} mol/L; SDS: 1×10^{-4} mol/L.

The calibration curve was linear in the range of $1.2 \times 10^{-7} – 3.6 \times 10^{-6}$ mol/L. When the signal noise ratio (SNR) was 3, the detection limit was 1.2×10^{-8} mol/L. The average recovery was 100.3 % (n = 3).

The electrooxidation of TC is rarely reported in the literature. This work has given an evidence and reasonable explanation of the oxidation TC at the acetylene black electrode in the presence of SDS. The system can be used as a sensitive and effective electrochemical method for the determination of TC.

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