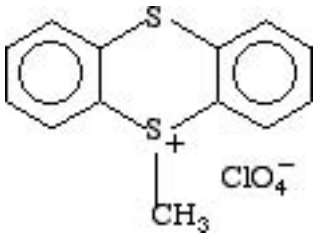
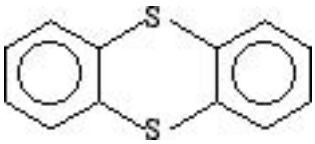
Fundamentals of Electrochemistry
CHEM*7234 CHEM 720
Assignment #4

Question 1: Figure 1 shows the reduction cyclic voltammogram of methyl-thianthrenium perchlorate (**1**) (2 mM) in $CH_3CN + NBu_4PF_6$ (0.1M) on a glassy carbon electrode at room temperature and at scan rate v = 0.2 V/s. Three reduction peaks are identified. The height of the 1st reduction peak corresponds to 60 μA, its peak width is equal to 70 mV. The last reduction peak corresponds to thianthrene (**2**). In the presence of a proton donor (phenol 2 mM), the height of the first peak doubles and the second peak disappears totally.



(1)



(2)

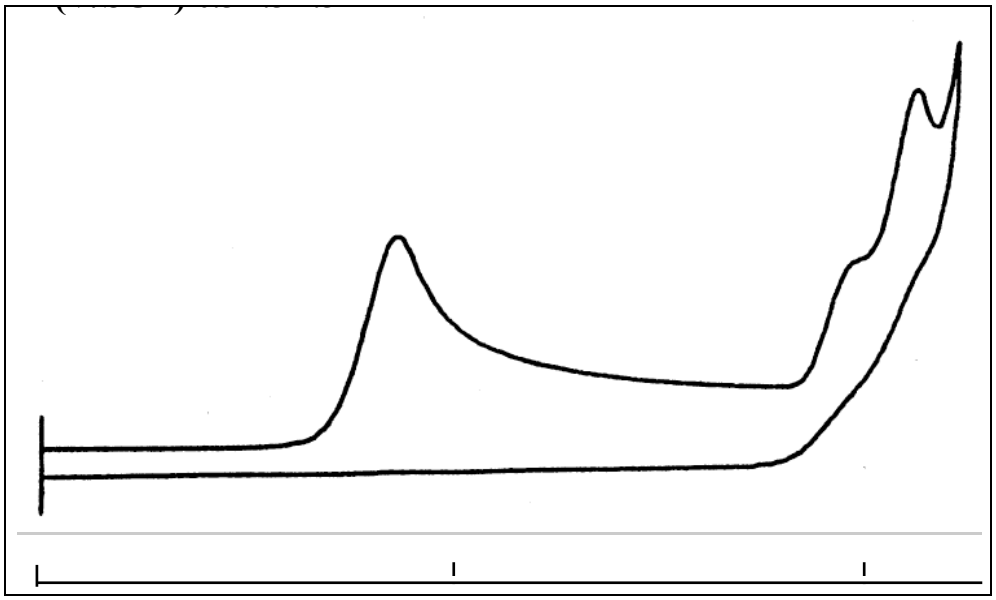


Figure 1: Cyclic voltammetry of methyl-thianthrenium perchlorate (**1**) (2 mM) in $CH_3CN + NBu_4PF_6$ (0.1M) on a glassy carbon electrode at room temperature and at a scan rate v = 0.2 V/s.

Knowing that the monoelectronic reversible oxidation peak of ferrocene (1mM) under similar conditions has a height equal to 29 μA. Determine:

a) The nature of the first electron transfer mechanism.
b) The expected slop of the variation of the first peak potential with the log of the scan rate (log (v)).
c) The number of electrons per molecule consumed at the first peak in the absence of phenol.
d) The nature of the product responsible for the second peak.
e) The global mechanism of the reaction in the absence and the presence of proton donor.
f) How would the CV look like if only 1 mM of phenol was added to the thianthrenium salt solution.

Question 2: Find the FALSE statement in the following and correct it:

To charge a Lead Acid Battery, the positive pole of the direct current source should be connected to the battery terminal with sign "+". Accordingly, the negative pole of the DC source should be connected to the battery terminal with sign "-". During the charging, the reduction of lead sulfate to "spongy" metallic lead occurs as the cathodic process. In the anodic process, lead sulfate transforms to lead dioxide. Charging is completed when the voltage between terminals reaches a maximum value (2.06V****n*** when the circuit is open and where ***n*** is the number of cells in the battery), the sulfuric acid concentration drops to a minimum (about 36%) and oxygen evolution occurs on the anode. In order to avoid hydrogen evolution and the formation of a highly explosive gaseous mixture, the capacity of the negative electrode is slightly higher than the positive electrode. As a result, when oxygen evolution starts on PbO_2, the negative electrode is not charged completely and oxygen diffuses through the electrolyte to be reduced on the cathode. This helps to maintain pressure inside the battery. However, after a long-time of lead-acid battery overcharging, the evolution of hydrogen (on negative electrode) and oxygen (on positive electrode) results in the formation of an explosive mixture of gases.

Question 3:

An experimental Direct Methanol Fuel Cell (single sell) is powered by a 2 molar methanol solution with a flow rate 0.8 $L \cdot h^{-1}$. The cell gives 0.9 V voltage at a current of 1A. What is the concentration of methanol in the out-coming flow if the anode power density is 100 mW cm^{-2} and the methanol crossover rate is 300 mA cm^{-2}? Changes in the water concentration can be neglected.