RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

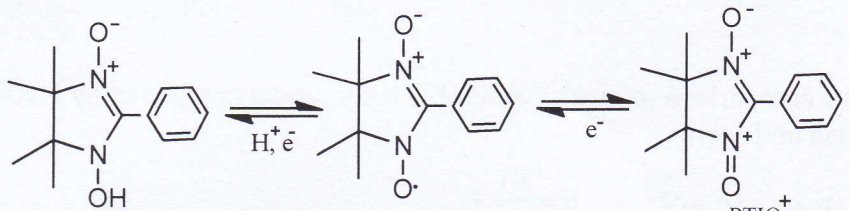
B.Sc. (Joint Major) Degree in Chemistry and Physics
Fourth Year – Semester II Examination – April / May. 2016

CHE 4202–Advanced Electrochemistry

Answer all **Four** questions Time allowed: Two hours

$R = 8.314\ J\ K^{-1}\ mol^{-1}, F = 96480\ C\ mol^{-1}$

1. The following reaction scheme describes how 2-phenyl-4,4,5,5,- tetramethylimidazoline -1-oxyl-3-oxide (PTIO) at pH 3.5 undergoes to $PTIO^+$ and PTIO-H at different potentials in a potential scanning between +900 mV and -100 mV *vs.* Ag/AgCl. Oxidation of PTIO to TIO^+ takes place at more positive potential compared to that of to PTIO-H.



PTIO-H PTIO $PTIO^+$

(a)

(i) Draw a likely cyclic voltammogram (CV) that you would expect from PTIO in10 mM phosphate buffer solution at a scan rate of 100 mV s^{-1} and state all the salient features of the CV.

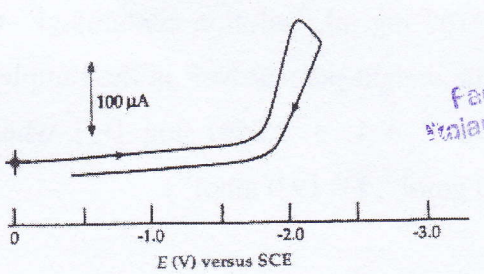
(ii) State the effect of (a) scan rate (b) concentration of PTIO and (c) pH on the CV of PTIO.

(iii) What is meant by diffusion controlled? How do you eliminate convection and migration currents in CV experiments?

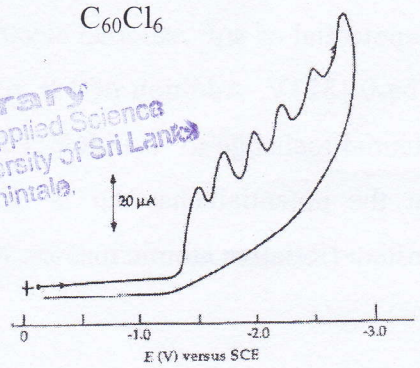
(iv) With the help of CVs, how do you experimentally show that oxidation of PTIO to TIO^+ is diffusion controlled

(b) Comment on the following CVsof two compounds recordedin dimethylformamide at a glassy carbon electrode.

n-Butyl iodide



$C_{60}Cl_6$



2. (a) Define the term (i) overpotential, η and (ii) exchange current, i_0 for a one electron reversible charge transfer process.

(b) Given that the Butler-Volmer equation for a one-electron transfer predicts how the observed current varies as a function of the overpotential and transfer coefficient, α.

$$i = i_0 \left\{ exp\left[\frac{-\alpha F\eta}{RT}\right] - exp\left[\frac{(1-\alpha)F\eta}{RT}\right]\right\}$$

The following data were obtained for the reaction $A + e^- \longrightarrow A^-$ in a solution at a 0.1 m^2 electrode at 298 K.

η/mV	-100	-120	-150	-500	-600
i/μA	45.9	62.6	100	965	965

Calculate (i) exchange current density, j_0 (ii) α and (iii) the charge transfer resistance, R_{ct} for the above cathodic reaction

3.(a)Give a qualitative comparison of electrical double layer models proposed by Helmholtz, Gouy-Chapman and Stern.

(b) At very low η values, ±50 mV $\eta = \frac{RT}{j_0 F} j$

The exchange current density for Pt/ $H_2(g)/H^+(aq)$ system at 298 K is 0.79 mA cm^{-2}. What current flows through a standard electrode of total area 5.0 cm^2 when the potential difference across the interface is + 5.0 mV?

4. (a) Explain how you would employ the rotating disk voltammetry or cyclic voltammetry for the determination of diffusion coefficient of an electroactive species.

(b) A 0.400 g sample of toothpaste was boiled with a 50 mL solution containing citrate buffer and NaClto extract the F^- ion. After cooling, the solution was diluted to exactly 100 mL. Thepotential of anF^-/calomel electrode system in a 25 mL aliquot of the sample was found to be-0.1823V. Addition of 5.0 mL of 0.00107 mg mL^{-1}solution containingF^- caused the potential tochange to -0.1446V. Calculate the weight-percent NaF in the sample assuming that the potentialbehaviour is of the form E = L + 0.0591 log [F^-] where L is a constant.(Relative atomic masses: Na = 23.0 $gmol^{-1}$, F= 19.0 $gmol^{-1}$)