



Register Number:

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**ST. JOSEPH'S COLLEGE - AUTONOMOUS, BENGALURU-27**  
**END SEMESTER EXAMINATION; NOVEMBER-2020**

**M. Sc. Chemistry – III Semester**

**CH-9318 ELECTROCHEMISTRY AND ELECTROANALYTICAL TECHNIQUES**

**Time: 2½ Hours**

**Max. Marks: 70**

*Note: This question paper has THREE parts and SEVENTEEN questions.*

**Part A**

**Answer any SIX of the following questions:**

**[2 x 6 = 12]**

- 1) What is an ideal polarized and an ideal non-polarized electrode?
- 2) Why is a three-electrode system used in voltammetry? Explain.
- 3) What is meant by the 'electrochemical window' of an electrode?
- 4) Distinguish between NPV and DPV techniques.
- 5) Discuss two essential properties of an ion-selective electrode.
- 6) What are electrocapillary curves? Explain
- 7) What is the polarization of an electrode? How is it quantified?
- 8) Explain the concept of 'triple ions' in solutions.

**Part-B**

**Answer any FOUR of the following questions:**

**[12 x 4 = 48]**

- 9) (a) Starting from Ficks' first law of diffusion, how do you arrive at Ilkovic's equation for average current at DME.  
(b) Plot the potential excitation signal and response signal in the following methods: i) LSV  
ii) staircase voltammetry  
(c) Explain anodic stripping voltammetry. (6+3+3)
- 10) (a) Describe the construction of the LaF<sub>3</sub> electrode and explain the mechanism of potential development and how it can be used to measure fluoride ion concentrations.  
(b) Write any three characteristics of capillary electrophoresis.  
(c) With relevant equations discuss electrical conductance across the glass membrane electrode (6+3+3)
- 11) (a) How do you apply the amperometric technique to determine the unknown concentration of the solute if the solute is Ba<sup>+2</sup> and the reagent is a sulphate?  
(b) With the help of a neat diagram, describe how a gas sensing probe could be used for the determination of CO<sub>2</sub> in a sample.

- (c) Explain the Helmholtz-Perin model with relevant expressions. (4+5+3)
- 12) (a) Obtain an expression for the potential of a dilute electrolyte.  
 (b) Obtain an expression for the mean ionic activity in the case of the following electrolytes:  
 (i)  $\text{Na}_2\text{SO}_4$  and (ii)  $\text{AlCl}_3$ . (8+4)
- 13) (a) Explain the variation of hyperbolic sine function at i) high overvoltage and ii) low overvoltage based on current density against overvoltage plot and with the help of the required expressions.  
 (b) What is bubble overvoltage? Discuss two factors affecting hydrogen overvoltage.  
 (c) What is specific adsorption? Explain.  
 (d) Explain the concept of surface excess. Derive an expression for it in terms of no of moles of species. (3+3+3+3)
- 14)(a) Discuss electrodics by deriving the Butler-Volmer equation.  
 (b) The following data were obtained from linear scan voltammetry of a reversible reduction reaction.

E Vs. SCE	I $\mu\text{A}$
-0.358	0.37
-0.372	0.95
-0.382	1.71
-0.400	3.48
-0.410	4.20
-0.435	4.97

The limiting current was  $5.15 \mu\text{A}$ . Show that the reduction reaction is reversible and determine the value of  $n$  and  $E_{1/2}$ . (7+5)

### Part-C

Answer any TWO of the following questions:

[5 x 2 = 10]

- 15) The solutions of each of the following species are given separately for investigation by linear sweep voltammetric method. Sydnone (-1.15V) Nitrostyrene (-0.62 V),  $\text{Ni}^{+2}$  (-0.25 V),  $\text{Cr}^{+3}$  (-0.41 V) and  $\text{Fe}^{+3}$  (+0.77 V). The values within parenthesis are their respective reduction potentials vs SCE. You are provided with the following electrodes to carry out appropriate electrochemical redox reactions—Mercury, gold, glassy carbon and platinum.
- i) Explain which one of these electrodes is suitable to investigate all the species mentioned above?
- ii) If the electrode's energy is increased, which one of them will undergo reduction first? Explain.

iii) If iron complexes to form ferricyanide ion, in which direction the potential of iron will shift on reduction? Give appropriate justification for your answer.

16) The following pair of electrolytes are given for analysis. a) 0.003 M BaCl<sub>2</sub> and 0.008 M CaCl<sub>2</sub>; which one of these will have a higher ionic strength? b) 0.003 M BaCl<sub>2</sub> and 0.003 M FeCl<sub>3</sub>; Which one of these has a higher mean activity coefficient. Justify your claim with relevant calculations.

17) a) Benzyl alcohol was present along with other cationic and anionic moieties in a mixture to be separated by capillary electrophoresis. Explain the effect on the migration of this molecule on i) increasing the pH of the electrolyte ii) decreasing the voltage.

b) Calculate the effective resistance across 1cm<sup>2</sup> of the following electrodes and identify the polarizable electrode:

(i) Pt, H<sub>2</sub>, H<sup>+</sup> ;  $i_0 = 0.85 \text{ mA cm}^{-2}$  and (ii) Hg, H<sub>2</sub>, H<sup>+</sup> ;  $i_0 = 0.75 \times 10^{-12} \text{ A cm}^{-2}$  (2+3)