Register Number:
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ST. JOSEPH'S COLLEGE - AUTONOMOUS, BENGALURU-27
SEMESTER EXAMINATION; NOVEMBER 2022
M. Sc. Chemistry – III Semester
CH 9322/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 causes anodic and cathodic currents in voltammetry?
2. In the cathodic stripping voltammetry, write the direction of potential applied in the pre-concentration step. What type of ions are determined by this method?
3. What is a potential window? How do you account for the potential window of the Hg electrode?
4. Before performing any experiment in the cathodic region, the solution is sparged with nitrogen. Why?
5. What do you understand if the symmetry factor is 0.75? Explain it with the help of a relevant Tafel plot.
6. Explain the electrode of the first kind with a suitable example.
7. How do you account for 'surface excess'? Explain.
8. Which among these M^+A^- and MAM^+ contribute to conduction? Explain.

Part-B

Answer any FOUR of the following questions: **[12 x 4 = 48]**

9. a) Applying the Nernst equation, discuss how a species's qualitative aspects (standard potentials) can be extracted from voltammograms.
   b) If the solute is electro-inactive and the reagent is electro-active, how do you apply the amperometric technique to determine the solute's equivalence point and unknown concentration?
   c) The fluoride electrode can only be used in the pH range of 5 to 8. Explain. (5+4+3)

10. a) Explain electroosmotic flow with a suitable diagram.
    b) Discuss capillary isotachophoresis used for the separation of proteins.
    c) Explain conductance across a glass membrane electrode (3+6+3)

11 a) Explain different modes of mass transport encountered in voltammetry.
   b) Write the diagnostic criteria for an electrochemically reversible system.

c) How do you reverse the electroosmotic flow? Explain.

d) Write any three characteristics of electroosmotic flow. (3+3+3+3)

12 a) Obtain an expression for the i) mean ionic activity for aluminum sulphate and ii) calculate the ionic activity coefficient of magnesium chloride if the ionic strength is 0.003.

b) i) Write Ilkovic's equation for maximum diffusion current. ii) Explain the basis for quantitative analysis of the analyte in polarography. iii) Discuss the significance of half-wave potential and diffusion current.

c) Prove that E_{ind} = Constant + 0.0592 log $[CO_2]_{\text{ext soln}}$ (4+5+3)

13 a) Discuss the limitation of the Helmholtz-Perrin model of the electrical double layer and explain the Gouy-Chapman model.

b) Derive the Lipmann equation. (4+8)

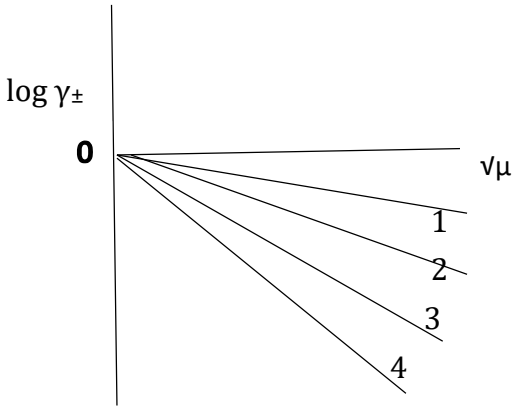
14 a) Derive the Butler-Volmer equation.

b) The exchange current density of $Pt/H_2/H^+$ is 0.79 mA cm^{-2} at 25 ^{0}C. Calculate the current density across it when the overpotential is i) 0.01V and ii) 0.2 V. Given: $\alpha = 0.5$. (8+4)

Part-C

Answer any TWO of the following questions: [5 x 2 = 10]

15.



Explain how you would assign the following electrolytes: (i) $CaSO_4$ ii) LiCl, iii) $AlCl_3$ iv) $ZnBr_2$ to the respective linear connections (1, 2, 3, and 4) in the accompanying figure using an appropriate theory.

16. a) The order of elution when using MEKC is vitamin B_3 (5.58 min), vitamin B_6 (6.59 min), vitamin B_2 (8.81min), and vitamin B_1 (11.21min). What conclusions can you make about the solubility of the B vitamins in the SDS micelle?

b) Telbin caries out a polarographic reduction of Zn^{+2}, Cu^{+2}, $Cd^{+2,}$ and Pb^{+2} in potassium nitrate by stripping voltammetric method using DME as the working electrode. He applies an anodic deposition potential under the unstirred condition at the rate of 15 mV s^{-1} for 120 seconds to pre-concentrate the ions at the surface of the working electrode. After allowing it to equilibrate for 10 seconds under

stirred conditions, he applies cathodic potential at a sweep rate of 50 mV s^{-1} with a pulse amplitude of 50 mV. Unfortunately, Telbin was unable to observe any stripping peaks. Identify any two major mistakes committed by Telbin which would justify that this experiment was not carried out according to the correct protocol. (3+2)

17 a) If the following equilibrium shifts to the left, can the silver bromide electrode be used to determine [Br^-] ion? Explain.

$AgBr + SCN^- \leftrightarrows AgSCN + Br^-$

b) Suppose a gold electrode is dipped in a solution containing Mo^{+5}, Sn^{+2}, Fe^{+2}, and MnO_4^{2-} ions in an appropriate supporting electrolyte. Standard electrode potentials are +0.48 V, +0.154 V, 0.771V, and +0.564 V, respectively. Write the order in which they are oxidized if the energy of the electrode is lowered. Justify your answer. (2+3)