Register Number:
Date:

ST. JOSEPH'S COLLEGE - AUTONOMOUS, BENGALURU-27

SEMESTER EXAMINATION: OCTOBER 2021

(Examination conducted in January-March 2022)

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) Using Fermi levels and frontier orbitals, explain how the reduction of species in solution takes place.
2) Explain concentration polarization.
3) In a polarogram, mark half-wave potential, maximum current, and average current.
4) Explain any one method to eliminate the charging current.
5) Discuss any two properties of ion-selective electrodes.
6) Explain surface excess.
7) Explain why the current fluctuates in a cyclic manner in polarographic experiments?
8) Write the Debye-Huckel-Bronsted equation and explain the terms.

Part-B

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

9) a) Discuss the application of voltammetry in determining equilibrium constants of coupled chemical reactions.
   b) What are triple ions? Discuss how the triple ions contribute to conduction.
   c) Distinguish between anodic and cathodic stripping voltammetry. (6+3+3)

10) a) Explain an electrophoresis method used to bring about the separation of amino acids.
    b) How do you reverse the electroosmotic flow? Explain.
    c) LaF_3 electrode cannot be used below pH 5 or above pH 8. Give reasons. (6+3+3)

11) a) How do you apply the amperometric technique to determine the unknown concentration of the solute, if the solute is electrochemically active and the reagent is electrochemically inactive?

    b) Explain two types of biocatalytic membrane electrodes used to determine BUN.

c) Distinguish between Helmholtz-Perrin model and Gouy-Chapman model of the double layer. (4+5+3)

12) a) Discuss the theory of ion association proposed by Bjerrum and discuss the conditions for ion association in solutions.

b) Obtain an expression for the mean ionic activity in the case of the following electrolytes: (i) Sodium borate and (ii) Zinc chloride. (8+4)

13) a) Derive Ilkovic's equation and obtain an expression for the average current.

b) If η=15 mV, I=70 mA through 2.5 cm^2 Pt electrode in H^+/H_2, What will be current density for η =100 mV assuming the symmetry factor = 0.5. (7+5)

14) a) Using relevant equations, discuss the necessity of sparging the solution in polarography.

b) Derive Lipmann equation. (4+8)

Part-C

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

15) A system in phosphate buffer was subjected to electrochemical investigation by cyclic voltammetry technique. The following data was recorded: A reversible peak with a difference of 0.059 V between the anodic and cathodic peak potentials, anodic peak current was proportional to $v^{½}$, i_{pa}/i_{pc} = 0.52. When KCN was used as a supporting electrolyte, and the energy of the electrode was increased, the peak potential shifted further, but when KNO_3 and KCl were used, the potential did not shift. From the above observations, answer the following questions:

i) Is the system electrochemically reversible?

ii) What is the number of electrons involved in the reaction?

iii) What was the nature of the electrochemical reaction (oxidation/reduction) carried out?

iv) Why did the potential shift in the case of KCN?

v) Can gold be used as a working electrode in this study? Account for your answer.

16) If the slope is $17.8V^{-1}$, calculate the transfer coefficient α and exchange current density i_0 for the discharge of H^+ on Pb. Given: the intercept -24.8; η =1V.

17) a) In a capillary zone experiment, a mixture of analytes A,B,C, and D is taken where A (molecular weight 176) and B (135) are positively charged, C is negatively, and D is neutral. What is their elution order if the capillary wall is coated with trimethylchlorosilane?

b) Based on the isoelectric point of the following compounds, predict the order of separation by the capillary isotachophoresis method. cytochrome c (10.7), lysozyme (11.1), trypsin (10.1), and trypsinogen (8.7). (2+3)