Registration Number:

Date & Session:

ST JOSEPH'S UNIVERSITY, BENGALURU -27

M. Sc. (CHEMISTRY) – III SEMESTER

SEMESTER EXAMINATION: NOVEMBER/DECEMBER 2023

(Examination conducted in Dec 2023)

CH 9323 – ELECTROCHEMISTRY AND ELECTROANALYTICAL TECHNIQUES

(For current batch students only)

Note: This paper contains THREE parts, SIXTEEN questions, and TW0 printed pages.

PART-A

Answer any EIGHT of the following questions: [2 x 8 = 16]

1. What is electrophoretic mobility? How is electrophoretic mobility related to the charge of the solute?
2. Briefly explain the mass transport by migration and how it is eliminated.
3. Explain the anisotropic nature of forces at the interface.
4. Which one of the following electrolytes has a higher ionic strength? i) 0.1 m NaCl and ii) 0.01 m $MgSO_4$.
5. What is bubble overvoltage?
6. Explain the problems encountered while using Hg electrodes in anodic and cathodic regions.
7. Explain normal pulse voltammetry with the help of relevant plots.
8. How do you account for the plateau observed in a polarogram?
9. What is the selectivity coefficient? What is the significance of the selectivity coefficient?
10. Draw the cross-sectional view of the structure of the glass membrane electrode.

PART-B

Answer any TWO of the following questions: [12 x 2 = 24]

11. a) Discuss how the mobilization of focused bands is carried out in the capillary isoelectrofocusing technique of separation.
    b) Derive an expression to determine the equilibrium constant of a coupled chemical reaction by applying the polarographic technique.
    c) Discuss how to determine the equivalence point using amperometric titration when the reagent produces a diffusion current and the solute is electro-inactive. (3+6+3)
12. a) Justify which of these has a lower mean ionic activity coefficient: 0.001 m $MgCl_2$ or 0.001 m $FePO_4$. (given the value for A=0.509].
    b) Derive the Debye-Huckel-Bronsted equation to account for the polarisation of the solvent molecules by the central ion.

c) Derive the Tafel equation starting from the Butler-Volmer equation. (4+3+5)

13. a) Applying the Nernst equation, discuss how the qualitative aspects (standard potentials) of a species can be extracted from voltammograms.
    b) Explain ideal polarizable and ideal non-polarizable electrodes with examples.
    c) Discuss any four factors influencing the degree of concentration polarization. (5+4+3)

PART-C

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

14. a) Elution time in minutes for some of the analytes are as follows in the MEKC technique: A=2.8, B =11.2, C=3.5, and D=6.0. Identify a completely hydrophobic neutral molecule.
    b) If the concentration of an external solution of hydrogen ions is 20 times more than the internal solution, what is the boundary potential developed? (3+2)

15. The following species undergo oxidation/reduction in the potential range +0.85 V to -1.0V in pH 5: Cd^{+2}, nitrostyrene, and methylene blue are to be reduced, whereas ascorbic acid, Ferrocyanide are to be oxidized. You have been provided with the following solid electrodes: Hg, Pt, and gold. Answer the following questions: i) Identify and justify your choice of suitable electrode material for the processes mentioned above for the respective molecules. ii) If glassy carbon is given, will you change your mind? Explain.

16. In a cyclic voltammetry experiment, molecule A was analysed using a carbon paste electrode. It was found to give a peak on the oxidation side at a potential of 0.365 V and a peak on reversing the scan at 0.275 V. How do you account for the following observations: i) On the reverse scan, if the peak current were to decrease what do you account it for? ii) Which electrochemical parameter gets affected by increasing the electrode size? iii) Does the peak potential get affected by an increase in scan rate? iv) What happens to capacitance current with an increase in the size of the electrode? Explain. v) What is the effect on peak potential difference if the scan rate is decreased?