48

RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Honours) Degree in Chemistry
B.Sc. (General) Degree in Applied Sciences

B.Sc. Third year Semester II Examination – February / March 2019
CHE 3311 – Advanced Analytical Chemistry II

Answer any six questions. **Time: 3 hours**
The use of a non-programmable calculator is permitted.

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1) (a) Explain clearly the difference between a distribution coefficient, K_D and a distribution ratio, D in a solvent extraction study of benzoic acid partitioning between the two liquid phases benzene and water. Find the relationship between K_D and D. (Assume the acid is monomeric in both solvents).

(30 marks)

(b) When an aqueous solution of $FeCl_3$ in conc. HCl is shaken with twice its volume of ether containing HCl, 99% of the iron is extracted. Calculate the distribution ratio of Fe(III). If 75 mL of aqueous HCl containing 0.360 g of Fe(III) is treated with 100 mL of ether, how many milligrams of iron are left in the aqueous phase?

(30 marks)

(c) Describe two principal solvent extraction systems for metal ions. Give one example of each.

A chelating agent, HT, dissolved in an organic solvent, used to extracts a metal, M^{2+} from an aqueous solution according to the reaction:

$$2H_2O + M^{2+}_{aq} + 2HT_{org} = MT_{2_{org}} + 2H_3O^+_{aq}$$

(i) Identify the equilibrium constant in terms of K_{D,MT_2}, $K_{a,HT}$, K_{f,MT_2} and $K_{D,HT}$

(ii) Calculate the pH if 75% of the metal is extracted from 10 mL of an aqueous phase with 10 mL of a 0.080 M solution of HT in the organic solvent.
(Hint: The equilibrium constant for this reaction is 0.10).

(40 marks)

2) (a) What are the limitations in liquid-liquid extractions and discuss briefly the methods to overcome the limitations.

(30 marks)

(b) Describe the different types of ion exchanger and their functional exchanger group. Briefly discuss the type of ion exchanger which is suitable for the separation of protein and peptides.

(40 marks)

(c) Explain the following interferences encountered during analysis by atomic absorption spectroscopy. Provide the solutions to minimize their contribution for each case of the following cases.

(i) Spectral interference.
(ii) Chemical interference.
(iii) Ionization interference.

(30 marks)

3) (a) Describe the following terms:

(i) Retention time.
(ii) Retention factor.
(iii) Selectivity factor.

(24 marks)

(b) The two species A, B are to be separated by elution with hexane in a column, packed with silica gel containing adsorbed water. The water/hexane distribution constants of A and B are 5.93 and 6.11 respectively and the ratio Vs/Vm for the packing is 0.398.

(i) Calculate the retention factor for each solute.
(ii) Calculate the selectivity factor.
(iii) How many plates are needed to provide a resolution of 1.5?
(iv) How long a column is needed if the plate height of the packing is 1.9×10^{-3} cm?

(v) If a flow rate of 6.50 cm/min is employed, how long will it take to elute the two species?

(50 marks)

(c) Discuss the normal phase and reverse phase chromatography? Predict the order of elution of the following compounds for a normal phase separation, and a reversed phase separation.

(i) n-hexane, n-hexanol, benzene.
(ii) ethyl acetate, diethyl ether, nitrobutane.

(26 marks)

4). (a) Describe the physical differences between open tubular column and packed column. What are the advantages and disadvantages of each?

(20 marks)

(b) Give one advantage and one limitation of each of the following gas chromatographic detectors, thermal conductivity detector, flame ionization detector, electron capture detector and photoionization detector.

(40 marks)

(c) List three variables that lead to band broadening and band separation in gas chromatography.

(24 marks)

(d) What is meant by temperature programming in gas chromatography?

(16 marks)

5). (a) Suggest reasons why analysis of vitamin C (ascorbic acid) is carried out with high performance liquid chromatography (HPLC) system and not with gas chromatography.

(20 marks)

(b) Discuss the use of derivatizing reagents in HPLC technique. Name two such reagents.

(20 marks)

(c) (i) List four requirements for the pumps used in HPLC.
(ii) Differentiate between isochratic and gradient elution.
(iii) Substances A and B have retention times of 16.40 and 17.63 minutes respectively on a 30.0 cm column. An unretained species passes the column in 1.30 minutes. The half peak widths $\left(W_{1/2}\right)$ for A and B are 0.56 and 0.61 minutes respectively. Calculate:
(1) The column resolution.
(2) Average number of theoretical plates.
(3) The plate height.

(60 marks)

6). (a) (i) A compound with a molar absorptivity of 3578 $dm^3\ mol^{-1}cm^{-1}$ (at 650 nm) exhibits an absorbance of 0.78 when placed within a 1 cm path length cuvette in a UV-VIS spectrophotometer. Calculate the molar concentration (M) of the compound.

(ii) The first excited state of Ca is reached by absorption of 422.7 nm light. Find the energy difference (kJ/mol) between the ground and excited states.
(Planck constant = 6.63×10^{-34} J s , speed of light = 3.00×10^{8} m s^{-1})

(30 marks)

(b) Calculate the Ksp for Hg_2Cl_2 if the standard potential of the calomel electrode is 0.268 V and that of Hg/Hg_2^{2+}, electrode is 0.789 V.
(2.303RT/F = 0.05916)

(30 marks)

(c) Traces of aniline can be determined electrochemically from bromide ion.

$$C_6H_5NH_2 + 3Br_2 \rightarrow C_6H_2Br_3NH_2 + 3H^+ + 3Br^-$$

The polarity of the working electrode is then reversed and the excess Br_2 is determined via a coulometric titration involving the generation of Cu^{2+} from Cu^+ in solution.

$$2Cu^+ + Br_2 \rightarrow 2Br^- + 2Cu^{2+}$$

Excess quantity of KBr and $CuSO_4$ were added to a 25.0 mL aqueous solution containing aniline. Calculate the mass of aniline in solution based on the following information:

Working electrode function	Generation time (s) with current 1.00 mA
Anode	226
Cathode	16.2

(Faraday's constant = 96485 C/mol, molar mass of aniline = 93 g/mol)

(40 marks)

7). (a) Write down the Randles-Sevcik equation and define the terms. Calculate the diffusion coefficient if the current is 1×10^{-5} A the area of the electrode is 2 mm^2 with a scan rate of 25 V/s and a concentration of 2.0 mM. (assume, n = 1)

(30 marks)

(b) Distinguish between:
(i) A working electrode and a reference electrode.
(ii) Faradaic current and non-faradaic current.

(iii) A residual current and a diffusion current.
(iv) Voltammetry and polarography.

(32 marks)

(c) (i) Discuss the advantages and limitations of dropping mercury electrode used in polarography. Give two applications of polarography.

(ii) In a polarographic reduction of Cd^{2+} to cadmium amalgam, Cd(Hg), the average value of the diffusion current for 2.00×10^{-4} M solution was found to be 1.34 μA for 3.0 s drop time. If the diffusion coefficient of Cd^{2+} is 8.56×10^{-6} cm^2/s. find the mass of mercury flowing through the capillary per unit time in mg/s.

(38 marks)

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