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UNIVERSITY OF RUHUNA – FACULTY OF ALLIED HEALTH SCIENCES

DEPARTMENT OF PHARMACY

FOURTH BPHARM PART I EXAMINATION – MARCH/APRIL 2021

PH 4123 PHARMACEUTICAL ANANLYSIS - SEQ

TIME: TWO HOURS

INSTRUCTIONS

- There are **four** questions in this paper.
- Answer all questions.
- No paper should be removed from the examination hall.
- Do not use any correction fluid.
- Use illustrations where necessary.

Part A

01.

1.1

1.1.1 Define the term "chemical shift" pertaining to ^{1}H NMR spectroscopy and mention why it is important in structure elucidation in organic molecules. (***10 marks***)

1.1.2 A peak is found at 1215 Hz in the ^{1}H NMR spectrum of acetylene measured in a 500 Mz NMR spectrometer. Calculate the chemical shift of this peak. (***05 marks***)

1.1.3 Explain how you would distinguish the following pairs of compounds using ^{1}H NMR spectroscopy. (***20 marks***)

a) 1-Chloropropane and 2-chloropropane

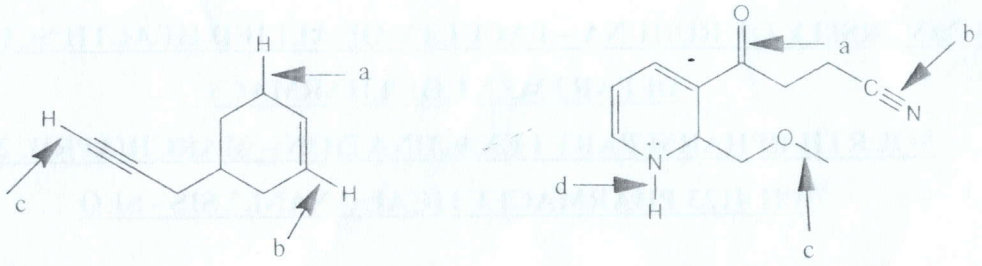
b) Propanal and propanone

1.1.4 The ^{1}H NMR spectrum of the carbonyl compound **P** ($C_4H_8O_2$) gives only three NMR signals: δ_1: 1.05 (triplet, 3H), δ_2: 2.35 (quartet, 2H), δ_3: 3.73 (singlet, 3H). Giving reasons suggest a plausible chemical structure for the compound **P**. (***15 marks***)

Part B

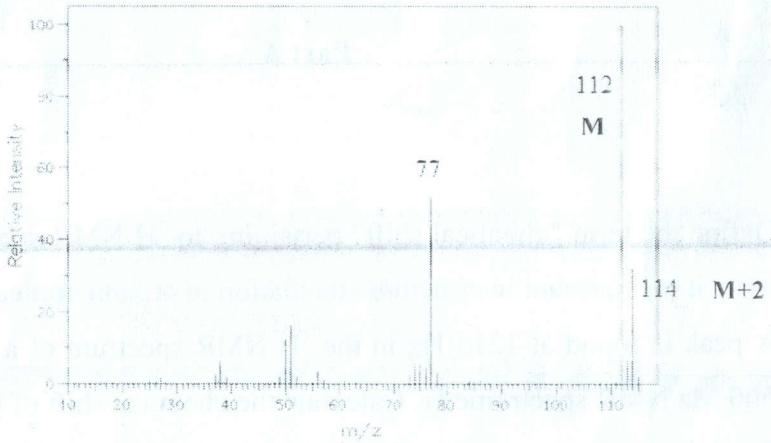
1.2

1.2.1 Rank the indicated bonds of the following two compounds in decreasing (highest to lowest) order of wavenumber in IR absorption. (***15 marks***)

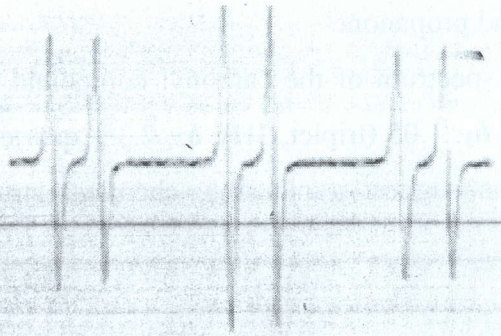


1.2.2 A compound with molecular formula $C_4H_8O_2$, shows absorptions at 2500-3300 (broad), 1720 and 1200 cm^{-1} in its IR spectrum. Propose possible structures for this compound and assign given absorption values to the corresponding bonds of your structure. ***(15 marks)***

1.2.3 Propose a structure for the compound having the following mass spectrum. Identify each of the labeled signals. ***(10 marks)***



1.2.4 The esr spectrum of hydroxymethyl radical $^{\bullet}CH_2OH$ is shown below. Explain the pattern of lines observed in the spectrum. ***(10 marks)***



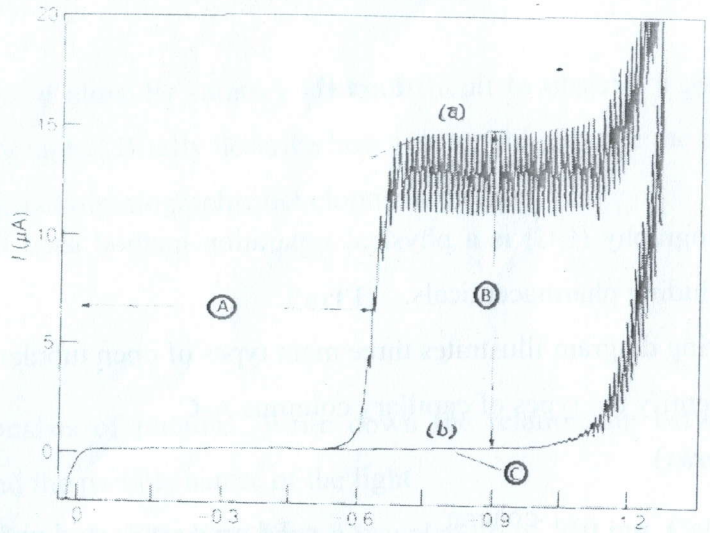
Part C

02.

2.1 Polarography is an electrolysis technique in which micro-electrolysis is performed at a dropping mercury electrode (DME) in an unstirred solution.

Answer the following questions using the polarogram obtained for (**a**) 1M solution of HCl containing 5 x 10^{-4} M Cd^{2+} and (**b**) 1 M solution of HCl.

(2)



2.1.1 Name **A**, **B** and **C** with brief descriptions. (***21 marks***)

2.1.2 Write down the chemical reaction pertaining to the polarographic wave.

(***07 marks***)

2.1.3 Following is a relation used in polarography.

$$i_d = 706nD^{1/2}m^{2/3}t^{1/6}c$$

2.1.3.1 Give the name of the above equation. (***06 marks***)

2.1.3.2 Using the above equation give the factors on which the current flowing in a DME depends. (***06 marks***)

2.1.4 Give the values of i_{max} and i_{avg} (***10 marks***)

2.2

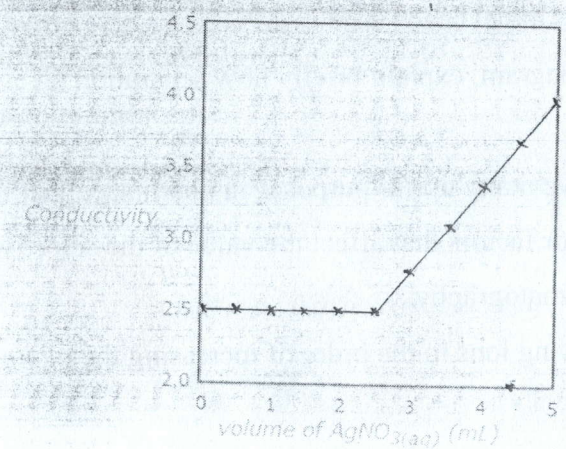
2.2.1 Name four common types of titrations. (***08 marks***)

2.2.2 Give common advantages of doing them conductometrically over the other methods. (***20 marks***)

2.2.3 Interpret the precipitation titration curve of KCl vs $AgNO_3$ given below.

(***22 marks***)

Note: conductivity of Cl^- and NO_3^- are 76.3 and 71.5 mol^{-1} cm^2 S respectively.



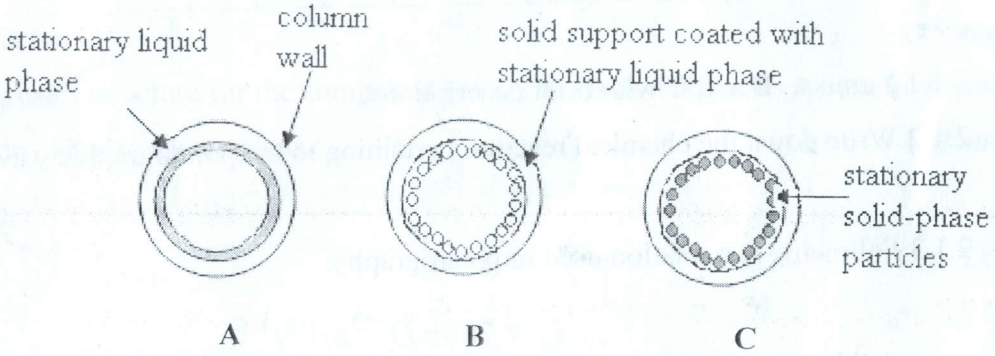
Part D

03.

3.1 Gas chromatography (GC) is a physical separation method used to separate volatile mixtures including pharmaceuticals.

3.1.1 Following diagram illustrates three main types of open tubular columns used in GC. Identify the types of capillary columns **A-C**.

(*12 marks*)



3.1.2 Calculate the linear flow velocity in cm/s for the following two GC columns.

3.1.2.1 A packed column with an inside diameter of 4.0 mm, the column porosity of 0.38, and the measured volumetric flow rate at the column outlet of 54.0 mL/min. (*10 marks*)

3.1.2.2 An open tubular column with an inside diameter of 0.19 mm and a volumetric flow rate of 0.87 mL/min. (*10 marks*)

3.1.3 Derivatization prior to analysis enables many more compounds to be analyzed by GC.

3.1.3.1 List four major reasons for derivatization. (*12 marks*)

3.1.3.2 What are the major methods used in derivatization. (*06 marks*)

3.2 Gel Permeation Chromatography (GPC) is one of the most important chromatographic techniques used to separate biopolymers.

3.2.1 List four properties of gel beads used in GPC. (*10 marks*)

3.2.2 Using a suitable diagram, explain briefly how separation takes place in GPC. (*15 marks*)

3.3 Ion exchange resins serve many useful purposes in pharmaceutical field.

3.3.1 Write the two major factors that affect the value of the selectivity coefficient in ion exchange chromatography. (*05 marks*)

3.3.2 Arrange the following ions in the order of increasing the rate of exchange. (*05 marks*)

Al^{3+}, Ca^{2+}, Th^{4+}, Na^{+}

3.4 Amino acids have close R_f values and are difficult to observe a good separation in paper chromatography. Briefly describe how you would improve the resolution of such a mixture using a chromatographic development method. ***(15 marks)***

Part E

04.

4.1

4.1.1 Light consists of photons. Write down the relationship between energy of a photon and the particle nature of the light. ***(10 marks)***

4.1.2 Photons in a pale blue light have a wavelength of 510 nm. Calculate the energy of a photon of this light. ***(10 marks)***

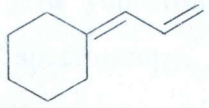
(h = Planck's constant = 6.625 10^{-34} Js, c = Speed of light = 2.998 × 10^8 m/s)

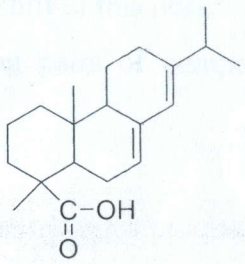
4.2

4.2.1. State the Beer-Lambert Law. ***(10 marks)***

4.2.2. A 5.50 x 10^{-5} M solution of potassium permanganate has a transmittance of 36.4% when measured in a 1.05 cm cell at a wavelength of 525 nm. Calculate the absorbance of this solution. ***(10 marks)***

4.3. Using Woodward-Fieser rules, calculate the λ_{max} for the following two compounds. ***(20 marks)***

4.3.1 

4.3.2 

4.4

4.4.1. Write down the processes that occur to give up the excess energy of an excited species by giving an example for each process. ***(20 marks)***

4.4.2. Write short accounts on following. ***(20 marks)***

4.4.2.1 Photoluminescence

4.4.2.2 Chemiluminescence

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