PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Synthesis of a derivative (NaHX) of the sodium salt of an organic acid

Apparatus:

1 beaker (250 cm^3), 2 beakers (50 cm^3), 1 pipette (10 cm^3; graduated at intervals of 0.1 cm^3), 1 measuring cylinder (50 cm^3), 1 capillary pipette (Pasteur pipette), 1 thermometer, 1 filter crucible (G4), apparatus for suction filtering, 1 glass rod.

Reagents:

Sodium salt of 1-naphtol-4-sulfonic acid (S), (sodium 1-naphtol-4-sulfonate), (M = 246.22 g mol^{-1}), sodium nitrite (M = 69.00 g mol^{-1}), aqueous solution of HCl (2 mol dm^{-3}), deionised water, absolute ethanol.

Procedure:

Mix the given lot of technical grade starting material, labelled I, (contains 1.50 g of sodium 1-naphtol-4-sulfonate, S) and 0.6 g of $NaNO_2$ with about 10 cm^3 of water in 50 cm^3 beaker. Cool in ice bath (a 250 cm^3 beaker) to the temperature 0 – 5 °C. Keeping the temperature in the 0 – 5 °C range, add dropwise 5 c m^3 of 2 M HCl (aq) to the reaction mixture. Stir for ten more minutes in an ice bath to effect the complete precipitation of the yellow-orange salt NaHX . n H_2O. Weigh the filter crucible accurately (± 0.5 mg). Filter the product with suction in the crucible and wash with a small amount (ca. 5 cm^3) of cold water and then twice (about 10 cm^3) with ethanol. Dry the product in the filter crucible at 110 °C for 30 minutes. Weigh the air-cooled anhydro us material together with the crucible and present it to the supervisor.

Calculate the percentage yield of NaHX (M = 275.20 g mol^{-1}).

The purity of the product NaHX influences your results in Problem 2!

Question:

Write the reaction equation using structural formulae.

PROBLEM 2 (practical)

The spectrophotometric determination of the concentration, acid constant K_{a2} and pK_{a2} of H_2X

Apparatus:

7 volumetric flasks (100 cm^3), 2 beakers (50 cm^3), 1 capillary pipette (Pasteur), 1 pipette (10 cm^3; graduated in intervals of 0.1 cm^3), 1 washing bottle, 1 glass rod, 1 container for waste materials, funnel.

Reagents:

Compound NaHX, aqueous stock solution of Na_2X (0.00100 mol dm^{-3}), aqueous solution of sodium perchlorate (1.00 mol dm^{-3}), aqueous solution of HCl (0.1 mol dm^{-3}), aqueous solution of NaOH (0.1 mol dm^{-3}).

Procedure:

a) Weigh accurately 183.5 ± 0.5 mg of NaHX and dissolve it in water in a volumetric flask and dilute up to the 100 cm^3 mark. Pipette 15.0 cm^3 of this solution into another 100 cm^3 volumetric flask and fill up to the mark with water to obtain the stock solution of NaHX. If you do not use your own material, you will get the NaHX from the service desk.

b) Prepare 5 solutions, numbered 1-5, in the remaining five 100 cm^3 volumetric flasks. These solutions have to fulfil the following requirements:
   - The total concentration of ($[X^{2-}] + [HX^-]$) in each solution must be exactly 0.000100 mol dm^{-3}.
   - The concentration of sodium perchlorate in each solution must be 0.100 mol dm^{-3} to maintain constant ionic strength. The solutions are prepared by pipetting into each volumetric flask 1-5 the accurate volumes of the NaHX and Na_2X stock solutions, adding a required volume of sodium perchlorate solution and filling up to the mark with water.

   - Solution 1 is prepared by pipetting the required amount of the stock solution of NaHX. Add ca. 3 cm^3 of HCl (aq) with the pipette to ensure that the anion is completely in the form HX^-, before adding the sodium perchlorate solution.

- Solution 5 is prepared by pipetting the required amount of the stock solution of Na_2X which is provided for you. Add ca. 3 cm^3 of the NaOH(aq) to ensure that the anion is completely in the form X^{2-}, before adding the sodium perchlorate solution.

- The three remaining solutions 2-4 are prepared by pipetting the stock solutions of NaHX and Na_2X in the following ratios before adding the sodium perchlorate solution:

Solution No.	Ratio NaHX(aq) : Na_2X(aq)
2	7 : 3
3	1 : 1
4	3 : 7

c) Take the five volumetric flasks to the service centre where their UV-vis spectra will be recorded in the region 300-500 nm for you. In another service centre the accurate pH of each solution will be recorded. You may observe the measurements.

d) From the plot of absorbance vs. wavelength, select the wavelength most appropriate for the determination of pK_{a2} of H_2X, and measure the corresponding absorbance of each solution.

e) Calculate the pK_{a2} of H_2X from the pH-absorbance data when the ionic strength I = 0.1 and the temperature is assumed to be ambient (25 ^oC). Note that:

$$K_{a2} = \frac{[H^+][X^-]}{[HX^-]} = \frac{c_{H^+} \times c_{X^{2-}}}{c_{HX^-}}$$

$$K_{a2} = \frac{(A\ A_{HX^-})[H^+]}{(A_{X^{2-}} - A)} \quad or \quad A = A_{x^{2-}} - (AA_{HX^-})\frac{[H^+]}{K_{a2}}$$

$$pf_{H^+} = \frac{0.509 \times \sqrt{I}}{1 + \sqrt{I}}$$

f) Which of your prepared solutions shows the largest buffer capacity? Calculate this buffer capacity, *P*, by any suitable method. You may use the equations given:

$$P = 2.3 \times \left([OH^-] + [H^+] + \frac{K_a [H^+] C}{(K_a + [H^+])^2} \right)$$

$$P = 2.3 \times \left(\frac{K_w}{[H^+]} + [H^+] + \frac{[X^{2-}][HX^-]}{C} \right)$$

C is the total concentration of the acid.

$K_w = 2.0 \times 10^{-14}$ at $I = 0.1$ and 25 °C.